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RESEARCH STUDIES IN NF_4^+ SALTS

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This report describes the results of a 3-year program in basic research studies in NF_4^+ chemistry. The mechanism of NF_4^+ salt formation and decomposition was determined and the decomposition kinetics of NF_4AsF_6 and NF_4BF_4 were measured. The formation of NF_3^+ salt intermediates, both in the formation and decomposition of NF_4^+ salts, was established, and the NF_3^+ radical cation was thoroughly

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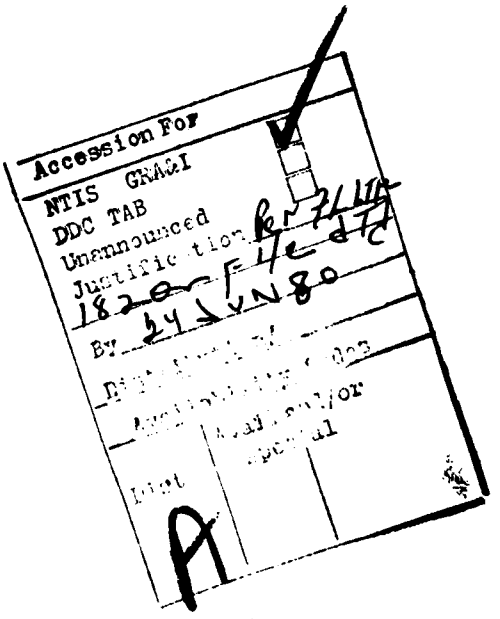
characterized by ESR spectroscopy. Improved synthetic methods were developed for NF_4SbF_6 and its metathesis to other NF_4^+ salts. A new method was developed for the synthesis of NF_4^+ salts derived from polymeric Lewis acids which do not form HF soluble cesium salts. The following new NF_4^+ salts were synthesized and thoroughly characterized: $(NF_4)_2MnF_6$, NF_4HF_2, NF_4UF_5O, NF_4ClO_4 and NF_4SO_3F. In addition, the novel $N_2F_3SnF_5$ and $N_2F_3SbF_6$ salts, which are useful burning rate modifiers in solid propellant NF_3-F_2 gas generator formulations, were prepared and characterized. Unsuccessful attempts were made to prepare NF_4NO_3, NF_4ClF_4O, NF_4BrF_4O, NF_4BrO_4 and NF_4^+ salts of several transition metal fluoride anions. Crystal structure determinations of NF_4BF_4 and NF_4SbF_6, and the measurement of thermodynamic data on NF_4BF_4, NF_4PF_6, NF_4AsF_6, and NF_4SbF_6 are in progress. The vibrational spectra of $^{14}NF_4^+$ and $^{15}NF_4^+$ were recorded and the measured isotopic shifts were used for the computation of a General Valence Force Field. Reliable methods were developed for the analyses of NF_4^+ salts.

FOREWORD

The research reported herein was supported by the U.S. Army Research Office under Contract No. DAAG29-77-C-0007, with Dr. B. Spielvogel as Scientific Officer. This is the final report for this contract and covers the period 1 April 1977 through 31 March 1980. The responsible scientist for this program was Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, W. W. Wilson, I. B. Goldberg, M. D. Lind, and Mr. R. D. Wilson, R. Rushworth and H. R. Crowe. The program was administered by Drs. K. O. Christe and L. R. Grant. Profs. R. Peacock, D. Russell and Dr. J. Fawcett of the University of Leicester, England, also contributed to the scientific effort.



CONTENTS

INTRODUCTION

This is the final report under Contract No. DAAG29-77-C-0007 and covers a 3-year period. It describes research related to NF_4^+ chemistry carried out in support of the Army's NF_3-F_2 gas generator programs. These NF_3-F_2 gas generators are based on solid propellant formulations, containing NF_4^+ salts as the principal ingredient, and are used for HF-DF chemical lasers. The objectives of this program included:

1. A study of the general formation and decomposition mechanism of NF_4^+ salts
2. The investigation of improved methods for the synthesis of known NF_4^+ salts
3. The synthesis of novel NF_4^+ salts
4. The characterization of known and novel NF_4^+ salts
5. The determination of the thermodynamic and structural properties of these salts

All of these objectives have been completed or, at least, partially accomplished and the results are summarized in this report. Because the bulk of the results have been summarized in the form of manuscripts, copies of which are given as Appendices to this report, the Technical Discussion is limited to a brief review of the major accomplishments.

It should be pointed out that most of the presently known NF_4^+ salts were discovered under ONR sponsorship (Ref. 1) resulting in a certain degree of overlap between these two programs.

PUBLICATIONS OF DATA GENERATED UNDER THIS CONTRACT

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17. "Synthesis and Characterization of NF_4ClO_4, $NF_4HF_2(xHF)$ and cis- and trans-
18. OIF_4OF," by K. O. Christe, W. W. Wilson, and R. D. Wilson, 9th International Symposium on Fluorine Chemistry, Avignon, France (September 1979), and 178th National ACS Meeting, Washington, D.C., September 1979.

19. An invited seminar on our research was given at the University of Southern California, 1979.

DISCUSSION

A. STATE OF THE ART OF NF_3-F_2 GAS GENERATORS

For a long time, nitrogen fluorides have been of great interest as advanced oxidizers for rocket propulsion. Of these, nitrogen trifluoride is the most important compound because it combines a high fluorine and energy content with a remarkable inertness. Its only major drawback is its low boiling point of -129 C. Therefore, the conversion of NF_3 into stable storable solids without significant loss in energy was highly desirable. The first step in this direction was undertaken in 1965 when one of us (Ref. 2) discovered the existence of the stable $NF_4^+AsF_6$ salt. However, it was not until 1971 when, with the advent of HF-DF chemical lasers, the interest in storable NF_3-F_2 sources was renewed.

It became rapidly obvious that NF_4^+ salts were the most promising oxidizers for solid propellant NF_3-F_2 gas generators. The concept of such a gas generator was conceived (Ref. 3) and, to a large extent (Ref. 4 through 11), developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers.

In an HF-DF chemical laser, F atoms are generated by burning F_2 in a precombustor with a fuel, such as hydrogen:

$$F_2 + H\cdot \longrightarrow HF + F\cdot$$

The F atoms are subsequently reacted with a cavity fuel, such as D_2, to produce vibrationally excited DF as the active lasing species:

$$F\cdot + D_2 \longrightarrow DF^* + D\cdot$$

In the original solid F atom generator concept (Ref. 3), the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need of a precombustor. This concept is demonstrated in the following equation for NF_4BF_4 with a small percentage of Teflon serving both as a fuel and a binder.

The heat of reaction (Q) is sufficient to dissociate most of the NF_3 and F_2 to F atoms and N_2:

$$NF_4BF_4 + (CF_2)_n \longrightarrow CF_4 + BF_3 + NF_3 + Q$$

$$2NF_3 + Q \longrightarrow N_2 + 6F\cdot$$

From a practical point of view, however, such a direct generation of F atoms is not desirable, since it does not allow the necessary flow controls and flexibility required for operation. Consequently, the concept was modified to that of an NF_3-F_2 molecule generator, using a gas catch tank. Further modification of this concept became necessary when system analysis data revealed that gaseous byproducts of high molecular weight and low C_p/C_v significantly degraded the performance of a laser. Consequently, an NF_3-F_2 gas generator was desired that would produce no gases other than NF_3 and F_2. The latter objective can be achieved by a so-called clinker system in which the BF_3 byproduct is converted by an alkali metal fluoride to a nonvolatile BF_4^- salt:

$$NF_4BF_4 + KF \longrightarrow KBF_4 + NF_3 + F_2$$

Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of KF lowers the NF_3-F_2 yield per pound of solid propellant and the possibility always exists of having incomplete clinkering.

Realizing these limitations, we have searched for novel NF_4^+ salts derived from nonvolatile Lewis acids. Further improvements in fluorine yields were achieved by the synthesis of salts containing more than one NF_4^+ cation per anion, i.e., salts containing multiply charged anions, and by the use of lighter anions which preferably were also oxidizers of their own, thereby contributing to the fluorine yields. The presently known NF_4^+ salts and their theoretical usable fluorine contents are summarized in Table 1.

TABLE 1. COMPARISON OF THE FLUORINE YIELDS OF PRESENTLY KNOWN NF_3-F_2 GAS GENERATOR SYSTEMS*

RANK	SYSTEM	THEORETICAL F, WT. PERCENT
1	$(NF_4)_2NiF_6$	64.6
2	$(NF_4)_2MnF_6$	59.9
3	$(NF_4)_2TiF_6$**	55.6
4	$(NF_4)_2SnF_6$	46.0
5	$(NF_4)_2TiF_6 \cdot 2.4KF$	39.5
6	$NF_4BF_4 \cdot 1.2KF$	38.5
7	$(NF_4)_2GeF_6 \cdot 2.4KF$	37.6
8	NF_4SnF_5	31.3
9	$NF_4PF_6 \cdot 1.2KF$	31.2
10	$NF_4GeF_5 \cdot 1.2KF$	29.0
11	$NF_4AsF_6 \cdot 1.2KF$	27.3
12	$NF_4SbF_6 \cdot 1.2KF$	24.0
13	$NF_4BiF_6 \cdot 1.2KF$	19.7

*THE MOLAR RATIO OF KF TO NF_4^+ SALT IS BASED ON EXPERIMENTAL DATA FOR NF_4BF_4 FORMULATIONS. A 20 MOLAR PERCENT EXCESS OF KF IS REQUIRED TO CLINKER BF_3 EFFICIENTLY.

**$(NF_4)_2TiF_6$ MIGHT REQUIRE CLINKERING WITH KF WHICH WOULD DROP ITS FLUORINE YIELD BELOW THAT OF $(NF_4)_2SnF_6$

Obviously, there were many problems associated with the development of this class of compounds, and the purpose of this program was to provide some of the required basic information. The following paragraphs summarize the results of our studies.

B. MECHANISM OF NF_4^+ FORMATION AND DECOMPOSITION

In order to develop improved and efficient methods for the synthesis of known and novel NF_4^+ salts, it was very important to gain a better understanding of the NF_4^+ formation mechanism. We have used ESR spectroscopy to show that the NF_3^+ radical cation is formed as an intermediate, not only in the γ-irradiation induced decomposition (Ref. 12) of NF_4^+ salts, but also in the UV photolyzed formation of NF_4^+ salts (Appendix A). Furthermore, we have measured the decomposition kinetics of NF_4BF_4 and NF_4AsF_6 (Appendix E), and found from the observed rate suppression data that both the formation and the decomposition of NF_4^+ salts are best explained by the following reversible mechanism given for NF_4AsF_6.

$$F_2 \rightleftharpoons 2\dot{F}$$

$$\dot{F} + NF_3 \rightleftharpoons \dot{N}F_4$$

$$\dot{N}F_4 + AsF_5 \rightleftharpoons \dot{N}F_3^+ + AsF_6^-$$

$$\dot{N}F_3^+ AsF_6^- + \dot{F} \rightleftharpoons NF_4^+ AsF_6^-$$

C. IMPROVED AND NOVEL SYNTHETIC METHODS

Because most of the advanced NF_4^+ salts are accessible only by metathetical methods, it was important to determine the most favorable reaction conditions. It was found that for the general process

$$NF_4^+A^- + M^+X^- \xrightarrow{\text{solvent}} NF_4^+X^- + MA\downarrow$$

the best product yields and purities are obtained when $A^-=SbF_6^-$, $M^+=Cs^+$, solvent = HF and the temperature of the filtration step is -78 C (Appendix B).

Improvements in the synthesis of the NF_4SbF_6 starting material were also made. It was found (Appendix F) that the compound can be prepared directly from the low cost and readily available SbF_3 starting material according to:

$$SbF_3 + 2F_2 + NF_3 \xrightarrow[30 - 70 \text{ atm}]{250\ C} NF_4^+SbF_6^-$$

A novel synthetic method was developed for NF_4^+ salts derived from nonvolatile polymeric Lewis acids which do not possess an HF soluble cesium salt. This method involves the reaction of the Lewis acid with an excess of NF_4HF_2 and was successfully demonstrated for $NF_4^+UF_5O^-$ (Appendix I) according to:

$$NF_4HF_2 + UF_4O \longrightarrow NF_4^+UF_5O^- + HF$$

D. SYNTHESIS OF NOVEL NF_4^+ SALTS

Several novel NF_4^+ salts were synthesized. These included $(NF_4)_2MnF_6$ (Appendix J), NF_4UF_5O (Appendix I), NF_4SO_3F (Appendix H), NF_4HF_2 and NF_4ClO_4 (Appendix G). The $(NF_4)_2MnF_6$ salt is, at the present time, the most promising candidate for a solid propellant NF_3-F_2 gas generator. Although its usable fluorine yield is not quite as high as that of $(NF_4)_2NiF_6$ (Table 1), its thermal stability is considerably higher, thus making it more useful. The low-temperature metathetical $CsSbF_6$ based process

$$Cs^+X^- + NF_4^+SbF^- \xrightarrow[-78\ C]{HF} CsSbF_6 \downarrow + NF_4^+X^-$$

was used for the syntheses of $(NF_4)_2MnF_6$, NF_4SO_3F, NF_4ClO_4 and NF_4HF_2. The NF_4UF_5O salt was prepared from NF_4HF_2 and UF_4O (see above). Theoretically, the NF_4ClO_4 salt would be of great interest as an ingredient in explosives, but unfortunately its thermal stability is too low for practical applications. Efforts were also made to prepare NF_4^+ salts containing the following anions, NO_3^-, ClF_4O^-, BrF_4O^-, $IF_4O_2^-$, BrO_4^-, and IO_4^- (Appendix G), and MF_6^{2-} or MF_6^{3-} anions derived from third row transition metal fluorides (Appendix J). Unfortunately, none of these salts was stable enough to permit their isolation.

The novel salts $N_2F_3^+SbF_6^-$ and $N_2F_3^+SnF_5^-$ were also prepared (Appendix G) according to:

$$N_2F_4 + SbF_5 \xrightarrow{HF} N_2F_3^+SbF_6^-$$

and

$$2N_2F_3^+SbF_6^- + Cs_2SnF_6 \xrightarrow[-78\ C]{HF} 2CsSbF_6 \downarrow + N_2F_3^+SnF_5^- + N_2F_4$$

These salts are stable and are of interest as burning rate modifiers in solid propellant NF_3-F_2 gas generator formulations containing NF_4^+ salts (Ref. 13).

E. CHARACTERIZATION OF NF_4^+ SALTS

The reliable determination of the properties of NF_4^+ salts is very important for practical applications. For example, the thermochemistry and densities of the NF_4^+ salts must be known for theoretical performance calculations. The thermal stability and decomposition mode must be known to decide whether certain salts pass long term storability requirements, and methods must be developed for determining the purity of the salts.

All the novel salts, described in the preceding paragraph, were thoroughly characterized. The techniques applied included elemental analyses (Appendix L), ^{19}F NMR, infrared, Raman and ESR spectroscopy, X-ray diffraction, DSC, thermal decomposition, and calorimetry. The results of these studies are given in the appendices, except for the crystal structure and calorimetric studies which are still under progress and will be completed under a follow-on contract. Two crystal structure studies on NF_4BF_4 and NF_4SbF_6, turned out to be rather frustrating, due to partial disorder of the anions. Both studies, however, indicate that the N-F bond length in NF_4^+ is about 1.25A, a value in excellent agreement with the results of our force field analysis (Appendix K). Attempts will be continued to refine these crystal structures. Thermodynamic data on NF_4BF_4, NF_4PF_6, NF_4AsF_6, and NF_4SbF_6 have been obtained by Prof. Peacock of the University of Leicester by measuring the heats of hydrolysis of these salts.

The results of these measurements will be crosschecked by Prof. Margrave of Rice University using a different technique.

F. CONCLUSION

This program has significantly advanced our knowledge of NF_4^+ chemistry. It has provided us with new synthetic methods, novel NF_4^+ salts and chemical, physical, structural, kinetic and thermodynamic data which have been and are extremely useful for the ongoing development work of solid propellant NF_3-F_2 gas generators.

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APPENDIX A

ESR EVIDENCE FOR THE FORMATION OF THE NF_3^+ RADICAL CATION AS AN INTERMEDIATE IN THE SYNTHESIS OF NF_4^+ SALTS BY LOW-TEMPERATURE UV PHOTOLYSIS

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304, and from the Science Center, Rockwell International, Thousand Oaks, California 91360

Electron Spin Resonance Evidence for the Formation of the NF_3^+ Radical Cation as an Intermediate in the Syntheses of NF_4^+ Salts by Low-Temperature Ultraviolet Photolysis

Karl O. Christe* and Ira B. Goldberg

Received July 18, 1977

The mechanism of the formation of NF_4^+ salts is of significant practical and theoretical interest. From a practical point of view, a better understanding of this mechanism would permit optimization of the reaction conditions for the direct syntheses of NF_4^+ salts, such as NF_4BF_4, NF_4PF_6, or NF_4GeF_5.[1] From a theoretical point of view, the formation of the NF_4^+ cation is intriguing[2] because its parent molecule NF_5 does not exist as a stable species. Since under the conditions used for most of the syntheses of NF_4^+ salts an F^+ cation should be extremely difficult, if not impossible, to prepare by chemical means, the following mechanism has previously been proposed[2] for the formation of NF_4AsF_6:

$$F_2 \xrightarrow{\Delta E} 2F\cdot \quad (1)$$

$$F\cdot + AsF_5 \rightarrow AsF_6\cdot \quad (2)$$

$$AsF_6\cdot + NF_3 \rightarrow NF_3^+AsF_6^- \quad (3)$$

$$NF_3^+AsF_6^- + F_2 \cdot \rightarrow NF_4^+AsF_6^- + F\cdot \quad (4)$$

In good agreement with the known experimental facts,[2] this mechanism requires only a moderate activation energy ($D°(F_2)$ = 36.8 kcal mol^{-1}).[3] The two critical intermediates are the $AsF_6\cdot$ radical and the NF_3^+ radical cation. Whereas the $AsF_6\cdot$ radical is unknown, the NF_3^+ radical cation was shown[4] to form during γ irradiation of NF_4^+ salts at −196 °C. Although this observation of the NF_3^+ cation demonstrated its possible existence at low temperature, it remained to be shown that the NF_3^+ radical cation is indeed formed as an intermediate in the syntheses of NF_4^+ salts. We have now succeeded in observing experimentally the NF_3^+ radical cation by ESR spectroscopy as an intermediate in the low-temperature UV photolyses of both the NF_3-F_2-AsF_5 and the NF_3-F_2-BF_3 systems. The results and implications derived from the observations are given in this paper.

Experimental Section

Binary and ternary mixtures of the starting materials were prepared for both the NF_3-F_2-BF_3 and the NF_3-F_2-AsF_5 systems in a stainless-steel Teflon FEP vacuum system. The sample tubes consisted of flamed-out quartz tubes of 4-mm o.d., 30-cm long, with a ballast volume of about 150 mL attached at the top. The starting materials were condensed into these tubes at −210 °C and the tubes were flame sealed. The NF_3 (Rocketdyne) was used without further purification, F_2 (Rocketdyne) was passed through a NaF scrubber for HF removal, and BF_3 (Matheson) and AsF_5 (Ozark Mahoning) were purified by fractional condensation prior to use. About 300 cm^3 of gas mixture was used for each sample tube in the following mole ratios: NF_3:F_2 = 1:10; BF_3:F_2 = 1:10; AsF_5:F_2 = 1:10; NF_3:BF_3 = 1:1; NF_3:AsF_5 = 1:1; NF_3:F_2:BF_3 = 1:4:1 and 1:2:1; NF_3:F_2:AsF_5 = 1:4:1.

The ESR spectra were recorded as previously described.[5,6] Variable-temperature control over the temperature range 4-300 K was achieved with an Air Products liquid-helium-transfer refrigerator, Model LTD110. For the photolyses, an Oriel Model 6240 arc lamp with a 200-W Hg lamp was used. In some of the experiments, the starting materials were condensed at −196 °C into the tip of the ESR tube and were irradiated for 10-30 min while inserted in a liquid-nitrogen-filled unsilvered Dewar. The ESR tube was then quickly transferred to the precooled ESR spectrometer. In other experiments, the sample tubes were irradiated at various temperatures inside the ESR cavity.

Results and Discussion

UV photolysis of both the NF_3-F_2-AsF_5 and the NF_3-F_2-BF_3 systems produced an intensely violet species which exhibited the ESR signal shown in Figure 1, traces A and B. Comparison with the previously published[4] anisotropic spectrum of the NF_3^+ cation (trace C, Figure 1) establishes beyond doubt the presence of NF_3^+ in our samples. The spectra are assigned on the basis of anisotropic hyperfine coupling to three fluorine atoms (I = $^1/_2$) and approximately isotropic hyperfine coupling to one nitrogen atom (I = 1). The **g** matrix is isotropic to within the line width. The spectra thus appear as a quartet of triplets as shown in Figure 1. The broader line widths observed in the spectra of UV-irradiated NF_3-F_2-AsF_5 and NF_3-F_2-BF_3 mixtures than in γ-irradiated NF_4SbF_6 may be the result of exchange or of dipolar interactions of materials on the surfaces of the solid components of the mixtures.

The observation of identical signals for both the BF_3- and the AsF_5-containing system proves that the signal must be due to a species not containing boron or arsenic. By carrying out irradiation experiments of the sample within the ESR cavity at −196 °C, it was shown that the signal strength increased during irradiation but did not decrease when the lamp was turned off. The thermal stability of the signal in the absence of UV radiation depended on the strength of the Lewis acid used. For the stronger Lewis acid AsF_5, the signal did not change significantly up to about −105 °C, whereas for BF_3 decomposition started at about −155 °C. When the sample tubes were warmed to ambient temperature, they contained white stable solids which were identified by Raman spectroscopy as NF_4AsF_6 and NF_4BF_4, respectively.[1,7,8] Irradiation of all possible binary mixtures, i.e., NF_3-F_2, Lewis acid-F_2, and NF_3-Lewis acid, under comparable conditions did not produce any ESR signal attributable to NF_3^+.

A positive identification of the proposed $AsF_6\cdot$ or $BF_4\cdot$ radical intermediates was not possible in the above experi-

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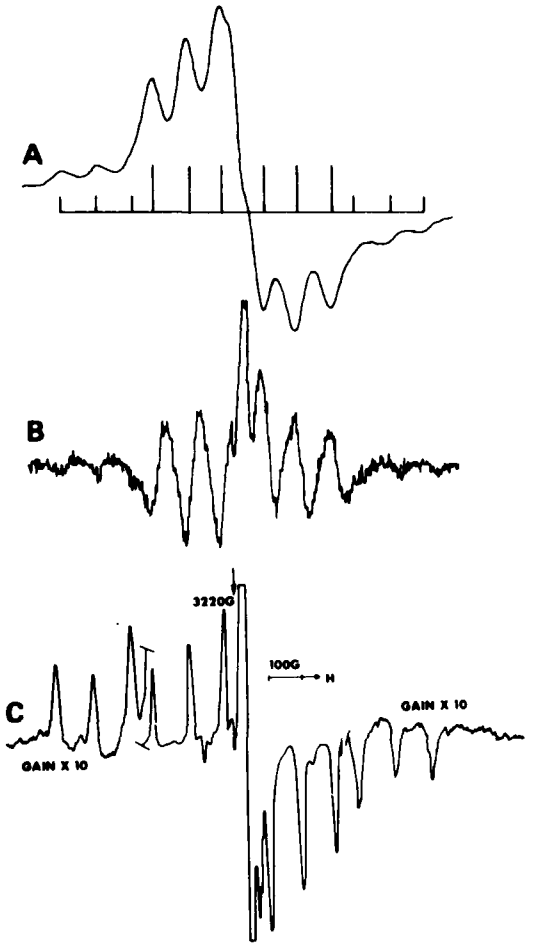

Figure 1. ESR spectra of the NF_3^+ radical cation obtained by UV photolysis of NF_3–F_2–BF_3 at −196 °C: trace A, first derivative; trace B, second derivative. For comparison, the known[4] first-derivative spectrum of NF_3^+ obtained by γ irradiation of polycrystalline NF_4SbF_6 at −196 °C is given as trace C.

ments. The observation of hyperfine splittings for the free AsF_6· or BF_4· radical at temperatures above several Kelvins is not likely because they would be in orbitally degenerate states which could cause rapid spin relaxation resulting in a strongly temperature-dependent line width. Furthermore, if we assume the existence of an AsF_6· or BF_4· radical in an ionic lattice, rapid electron exchange between the radicals and the corresponding anions is possible which would destroy hyperfine structure. The line width of the resulting signal would depend on the rate of exchange. Finally, in our experiments we were dealing with polymeric solid AsF_5 or BF_3 phases which on combination with a fluorine radical are not likely to result in an isolated AsF_6· or BF_4· radical. In our experiments, several ESR signals were observed in addition to NF_3^+. However, in the absence of observable hyperfine structure we prefer not to make any assignments.

On the basis of our results, the following conclusions can be reached concerning the formation mechanism of NF_4^+ salts. (i) The NF_3^+ radical cation is indeed an important intermediate. (ii) The requirement of UV activation and of both F_2 and a Lewis acid for the synthesis of NF_3^+ is in agreement with steps 1 and 2 of the given mechanism. (iii) The strength of the Lewis acid determines the thermal stability and lifetime of the intermediate NF_3^+ salt formed. This can account for the low-temperature conditions required for the synthesis of the NF_4^+ salts of weaker Lewis acids. (iv) In the absence of UV irradiation, the NF_3^+ salts do not spontaneously react with the large excess of liquid F_2 present. This indicates that in the absence of an activation energy source the thermodynamically feasible[2] chain-propagation step $NF_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F$· does not play an important role. Possibly, the conversion of $NF_3^+AsF_6^-$ to $NF_4^+AsF_6^-$ may require F· atoms according to

$$NF_3^+AsF_6^- + F\cdot \rightarrow NF_4^+AsF_6^- \qquad (5)$$

Since the intermediate NF_3^+ salt is an ionic solid, its reaction with a fluorine atom might well be a heterogeneous diffusion-controlled reaction and step 5 might be the rate-determining step in the mechanism. It was shown that at temperatures above −196 °C, where a given NF_3^+ salt is still stable in the absence of light, UV irradiation causes a rapid decay of the NF_3^+ ESR signal. However, it was not possible to distinguish whether this decay was caused by photodecomposition of the intermediate NF_3^+ salt or by the reaction of the latter with the generated F· atoms according to step 5.

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Registry No. NF_3^+, 54384-83-7; NF_4AsF_6, 16871-75-3; NF_4BF_4, 15640-93-4.

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APPENDIX B

ON THE SYNTHESES AND PROPERTIES OF SOME HEXAFLUOROBISMUTHATE (V) SALTS AND THEIR USE IN THE METATHETICAL SYNTHESES OF NF_4^+ SALTS

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ON THE SYNTHESES AND PROPERTIES OF SOME HEXAFLUOROBISMUTHATE (V) SALTS AND THEIR USE IN THE METATHETICAL SYNTHESIS OF NF_4^+ SALTS

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SUMMARY

The salts $LiBiF_6$, $NaBiF_6$, $KBiF_6$, $CsBiF_6$ and NF_4BiF_6 were prepared and characterized. Differences in the observed numbers and relative intensities of some of the Raman bands of these salts are explained by crystal effects. Solubilities of these salts in anhydrous HF at -78° were determined and compared to those of the corresponding SbF_6^- salts. It was shown that, contrary to a previous report, $CsBiF_6$ does not exhibit any unusual properties such as forming a mushy volatile HF adduct. The potential of NF_4BiF_6 based metathetical processes for the production of other NF_4^+ salts was evaluated. The novel $H_3O^+BiF_6^-$ salt was prepared and characterized. The usefulness of BiF_5 for water removal from HF is briefly discussed.

INTRODUCTION

In the course of our work on oxonium salts [1] and metathetical NF_4^+ salt processes [2-6], we became interested in pentavalent bismuth compounds as possible replacements for the corresponding antimony compounds. For example, the use of the less volatile BiF_5 has been proposed [1], but has never been tested, as an alternative to SbF_5

for removal of small amounts of water from HF. Because NF_4BiF_6 has become readily accessible by direct thermal synthesis from NF_3, F_2, and BiF_5 [7], it holds potential as a starting material in metathetical processes for the production of other less accessible NF_4^+ salts. However, its usefulness in such a process depends on the relative solubilities of its salts in a suitable solvent, such as anhydrous HF. Although BiF_6^- salts have been known [8] since 1950, only a small number of papers [7, 9-18] dealing with BiF_6^- salts have been reported since then, and some of the reported data are very much open to question. For example, Surles and coworkers reported [13] that HF formed a stable adduct with $CsBiF_6$ and that this adduct readily sublimed on heating. Consequently, a more systematic study of BiF_6^- salts was necessary in order to be able to properly evaluate the potential of BiF_6^- salts in the above applications.

EXPERIMENTAL

Materials and Apparatus

The apparatus, handling procedures, and the method used for the HF drying have previously been described [1,6]. Bismuth pentafluoride (Ozark Mahoning Co.) did not contain any detectable impurities and was used as received. Antimony pentafluoride (Ozark Mahoning Co.) was distilled prior to use. Lithium fluoride (Baker, A. R.) and NaF (MCB, Reagent grade) were used as received. Potassium fluoride (Allied, Reagent grade) and CsF (KBI) were dried by fusion in a platinum crucible and powdered in the drybox. The syntheses of NF_4BiF_6 [7] and NF_4SbF_6 [4] have previously been described. Except for $NaBF_4$ which was obtained from H_3BO_3 and Na_2CO_3 in concentrated aqueous HF solution, all the alkali metal tetrafluoroborates were prepared by introducing a slight excess of gaseous BF_3 into stirred solutions of the corresponding alkali metal fluorides in anhydrous HF at 20°, followed by removal of the volatile products.

Syntheses of BiF_6^- and SbF_6^- Salts

For the syntheses of the alkali metal hexafluorobismuthates, equimolar amounts of finely powdered alkali metal fluoride and BiF_5 were heated in a Monel cylinder for several days to 280° under 2 atm

of F_2. The vibrational spectra of the resulting products showed no evidence for the presence of either unreacted BiF_5 [19] or polybismuthate salts [7]. When these reactions were carried out at 150°, however, the products contained some polybismuthate salts. The alkali metal hexafluoroantimonates were prepared in a similar manner by heating equimolar mixtures of SbF_5 and the corresponding alkali metal fluoride in a F_2 atmosphere to 280°. Again, vibrational spectra of the solid products showed no evidence for the presence of polyantimonates.

Spectra

Infrared spectra of solids were recorded as dry powders between pressed AgCl or AgBr disks on a Perkin Elmer Model 283 spectrometer. Raman spectra were recorded in glass melting point, quartz or Kel-F capillaries on a Cary Model 83 spectrophotometer using the 4880Å exciting line of an Argon ion laser. Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel filtered copper Kα radiation and quartz capillaries as sample containers. The thermal decomposition of salts was examined with a Perkin Elmer differential scanning calorimeter (Model DSC-1B) using crimp-sealed aluminum pans as sample containers and a heating rate of 2.5°/min at atmospheric pressure.

Solubility Measurements

Solubilities of the salts in anhydrous HF at -78° were measured in an apparatus similar to that previously described [6] for metathetical reactions, except for eliminating trap I. Saturated solutions were prepared at -78° and separated from excess undissolved salt by filtration at -78°. The HF solvent was pumped off at ambient temperature, and the amount of HF used and of the solid residues obtained after HF removal were determined by weighing.

Metathetical Reactions

Metathetical reactions between NF_4BiF_6 or NF_4SbF_6 and different alkali metal tetrafluoroborates in anhydrous HF solution were carried out as previously described [4,6].

Synthesis of H_3OBiF_6

Bismuth pentafluoride (10.08 mmol) was transferred in the glove box into a passivated (with ClF_3) Teflon FEP ampule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10.12 g) which had been stored over BiF_5 was condensed into the ampule at -196°. The mixture was warmed to room temperature, and the Raman spectrum of the resulting clear solution was recorded. It showed bands similar, but not identical, to those expected for either BiF_6^- (see below) or solid BiF_5 [16, 19]. The ampule was cooled to -196°, and distilled H_2O (10 mmol) was syringed into the ampule. On warm up to ambient temperature, a copius white precipitate was formed. The mixture was stirred for ten hours at 25°. The Raman spectrum of the clear solution above the white solid precipitate showed the bands characteristic for BiF_6^- (see below). Removal of the HF solvent in a dynamic vacuum at -45° resulted in the formation of a white solid (3.469g, weight calcd for 10.08 mmol of H_3OBiF_6 = 3.447g) which was identified by Raman and infrared spectroscopy as $H_3O^+BiF_6^-$. This solid was stable at ambient temperature only under an HF pressure of about 20mm. On evacuation of the ampule, the white solid would immediately turn dark brown. When the valve of the ampule was closed to allow the pressure to build up again, the white color of the sample was restored. Complete decomposition of H_3OBiF_6 in a dynamic vacuum at 35°for 3 days resulted in a light cream colored solid. Based on its weight, physical properties (nonhygroscopic, insoluble in H_2O and aqueous HCl, sublimination at the softening point of glass), and elemental analysis (found: Bi, 77.2; F, 23.3; O, 0.2; calcd for BiF_3: Bi, 78.57, F, 21.43; O, 0) this solid appeared to be mainly BiF_3. The vibrational spectra of the solid decomposition product did not show any evidence for the presence of either H_3O^+ or BiF_6^-.

RESULTS AND DISCUSSION

Syntheses and Properties of Hexafluorobismuthates

The alkali metal hexafluorobismuthates were prepared from equimolar amounts of BiF_5 and the corresponding alkali metal fluoride by heating to 280° in a Monel cylinder. Fluorine was added to the

cylinder to suppress possible decomposition of BiF_5 to BiF_3 and F_2. This synthesis is similar to that [9] previously reported, except for using a significantly higher temperature. Using the previously reported [9] temperature conditions (85-150°), the product always contained some polybismuthate salt. For the syntheses of the alkali metal hexafluoroantimonates, similar reaction conditions were required to suppress the formation of polyantimonates.

The rather unusual properties previously reported [13] for $CsBiF_6$ could not be confirmed. Thus, $CsBiF_6$ was quantitatively recovered from HF solutions by pumping at ambient temperature, without any evidence for the formation of a stable $CsBiF_6 \cdot xHF$ adduct. Furthermore, no evidence was found for sublimation without decomposition for either HF treated or untreated $CsBiF_6$. DSC data obtained for $CsBiF_6$ showed a small reversible endotherm at 190°, attributed to a phase change, and the onset of a large endotherm at 308°, attributed to decomposition. Thermal decomposition of $CsBiF_6$ around 300° was confirmed by visual observation of samples sealed in melting point capillaries. At this temperature, sublimation of BiF_5 to the colder parts of the capillary occurred. For comparison, DSC data were also recorded for $CsSbF_6$. They showed a small reversible endotherm (phase change) at 187° and the onset of endothermic decomposition at 296°. These data show that the thermal stabilities of $CsSbF_6$ and $CsBiF_6$ are similar, with the bismuth salt being slightly more stable.

The vibrational spectra of the alkali metal hexafluorobismuthates were also recorded and showed some remarkable differences (see Figure 1). Particularly, the Raman active deformation mode exhibited different numbers of bands and intensity ratios. In order to determine whether the observed splittings were caused by the simultaneous presence of more than one crystal modification, the Debye-Scherrer powder patterns of these compounds were recorded In excellent agreement with a previous report [10], it was found that $LiBiF_6$ and $NaBiF_6$ were rhombohedral ($LiSbF_6$ type), $KBiF_6$ was cubic (low-temperature α-modification), and $CsBiF_6$ was rhombohedral ($KOsF_6$ type). No evidence was found for the presence of other modifications in either the thermally prepared (230°) or the HF recrystallized (-78°) samples. The observed splittings can be readily explained, however, by solid state effects. In the rhombohedral compounds (space group $R\bar{3}$-C_{3i}^2, Nr. 148, 1 molecule per Bravais cell [10]), the site symmetry of BiF_6^- is C_{3i}.

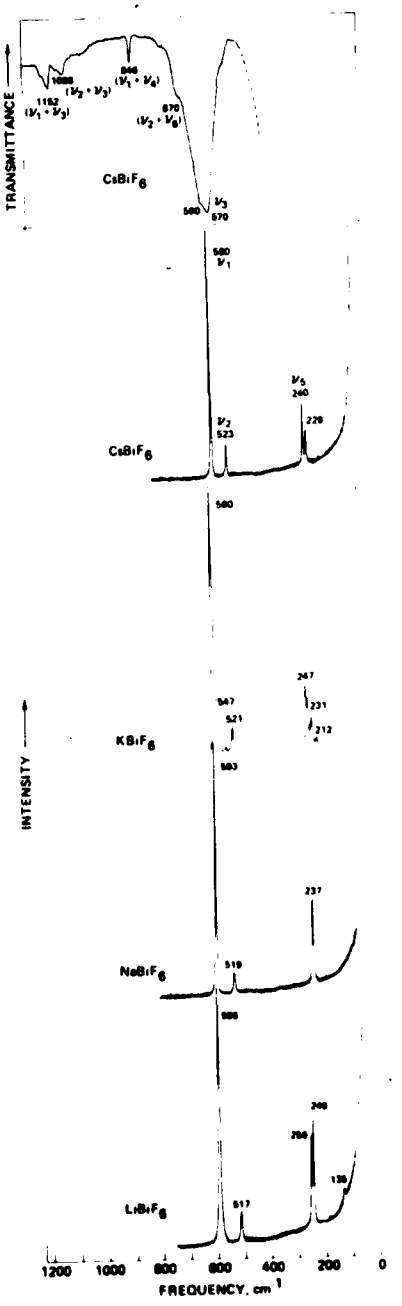

Figure 1.

Infrared spectrum of $CsBiF_6$ and Raman spectra of $CsBiF_6$, $KBiF_6$, $NaBiF_6$, and $LiBiF_6$. The infrared spectrum was recorded as a dry powder between pressed AgCl disks. The broken line is due to absorption by the window material.

TABLE I.

Correlation Table for Isolated BiF_6^- of Point Group O_h and for Site Symmetry C_{3i}

O_h	C_{3i}
A_{1g}	A_g
E_g	E_g
F_{2g}	$A_g + E_g$
F_{1u}	$A_u + E_u$
F_{2u}	$A_u + E_u$

Therefore, from Table I only the F_{2g} mode in the Raman and the F_{1u} modes in the infrared are expected to be split into two components. For cubic $KBiF_6$ (space group Ia3, Nr. 206) the site symmetry of BiF_6^- is again C_{3i}, but since the Bravais cell contains four molecules, factor group splitting can further cause the doubly degenerate E_g modes to split into two components. These predictions are in good agreement with our observations (see Figure 1), except for $NaBiF_6$ which exhibits only one Raman band in the BiF_6^- deformation region. This lack of splitting for $NaBiF_6$ is attributed to a coincidence of the frequencies of the A_g and the E_g components of ν_5. This is plausible since the weaker (probably the E_g) component has a higher frequency in $LiBiF_6$ and a lower frequency in $CsBiF_6$ than the more intense (probably the A_g) component. The frequency separation of the two components in $NaBiF_6$ must be rather small since, even at a spectral slit width of 1 cm^{-1}, we could not resolve the band into two components.

The infrared spectrum of $CsBiF_6$ (see Figure 1) shows a very intense and broad band for the antisymmetric BiF_6^- stretching mode ν_3 (F_{1u}) at 570 cm^{-1}. It exhibits a pronounced shoulder at 590 cm^{-1} which probably represents the second component of ν_3 predicted for C_{3i} symmetry (see Table 1). In addition, several infrared allowed combination bands were observed (see Figure 1). From these, the frequencies of the two remaining deformation modes can be derived as: $\nu_4(F_{1u})$ = 277 and $\nu_6(F_{2u})$ = 147 cm^{-1}. It should be noted that the combination bands involving ν_3 show splittings of about 20 cm^{-1}, analogous to that exhibited by ν_3 itself. This lends further support to the above assignments.

The previously reported [16] Raman spectrum of $NOBiF_6$ exhibits the same splittings and intensity pattern as α-$KBiF_6$, indicating that the two compounds are probably isotypic. Of the six frequency values reported by Bougon and coworkers [14] for BiF_6^-, ν_4 and ν_5 appear too low and should be revised. In agreement with a previous report [7], it was found that infrared spectroscopy is well suited for the detection of polybismuthate impurities in BiF_6^- salts. The polyanions result in an intense infrared band at around 440 cm^{-1}.

Solubility Measurements

The metathetical production of NF_4^+ salts is based on the following principle. A readily available and highly soluble NF_4^+ salt, such as NF_4SbF_6, is reacted in a suitable solvent, such as anhydrous HF, with an alkali metal salt containing the desired anion. If the alkali metal is chosen in such a manner that the starting materials and the desired NF_4^+ salt product are highly soluble and the resulting alkali metal SbF_6^- salt, for example, is of very low solubility, the following general equilibrium, where X=Sb, can be shifted far to the right hand side:

$$MY + NF_4XF_6 \xrightarrow{HF} MXF_6\downarrow + NF_4Y$$

The principle has been demonstrated for salts where Y = BF_4^- [2-4], SnF_6^{2-} [6], TiF_6^{2-} [5], and NiF_6^{2-} [20]. Prior to now, X had always been Sb; but the case where X could be Bi had not been tested. Since NF_4BiF_6 has recently become readily available by direct synthesis [7], and since an extrapolation of crude solubility data, previously measured [2] for alkali metal XF_6^- salts (X=As, Sb) in HF at room temperature, indicated that $LiBiF_6$ might possess the lowest solubility of any MXF_6 salt, quantitative solubility data for MXF_6 salts in anhydrous HF were desired. These data should allow to determine whether a BiF_6^- based process would offer any significant advantages over one based on SbF_6^-.

The solubilities of NF_4^+ and of several alkali metal BiF_6^- and SbF_6^- salts were measured in anhydrous HF at -78°. The low temperature was chosen based on our past experience [4]. The results of our measurements are summarized in Table II. As can be seen, the measured solubilities clearly favor a process based on a cesium rather than a

lithium salt. Furthermore, the solubility of $CsBiF_6$ is only slightly lower than that of $CsSbF_6$, thus not compensating for the significantly lower solubility of the NF_4BiF_6 starting material in HF and its less favorable formation rate [7], compared to those of NF_4SbF_6 [4]. Consequently, based on all the presently available experimental data, a $CsSbF_6$ based process appears to be the most attractive method for the metathetical preparation of other NF_4^+ salts.

TABLE II

Solubilities of Various BiF_6^- and SbF_6^- Salts in Anhydrous HF at -78°

Anion / Cation	SbF_6^-		BiF_6^-	
	a	b	a	b
NF_4^+	259.0	0.7951	173.1	0.4191
Li^+	9.21	0.0379	11.9	0.0361
Na^+	7.48	0.0289	25.6	0.0740
K^+	c	c	20.2	0.0558
Cs^+	1.80	0.00488	1.71	0.00373

a) in mg of solute per g of HF

b) in mole of solute per 1000g of HF

c) not measured

Metathetical NF_4BF_4 Production

Since in the metathetical production of NF_4BF_4 highly concentrated HF solutions are used, the activity coefficients of the ions are expected to differ significantly from those of the more dilute solutions of the solubility measurements. Consequently, the knowledge of solubility data is insufficient to predict accurately the product composition obtainable from metathetical experiments.

Metathetical NF_4BF_4 production runs using different MBF_4 and NF_4XF_6 salts in HF were carried out. Typical results from such experiments are shown in Table III. As can be seen, the data of Tables II and III are only in qualitative, but not quantitative, agreement. As

TABLE III.

Comparison of the Composition of the Crude Products Obtained by the Metatheses of NF_4^+ Salts with Different Alkali Metal Tetrafluoroborates in HF at -78°

System[a]	Composition of Product (weight %)		
	NF_4BF_4	NF_4XF_6	MXF_6
$LiBF_4$ - NF_4SbF_6	81.7	8.4	9.9
$LiBF_4$ - NF_4BiF_6	86.7	5.9	7.4
$NaBF_4$ - NF_4SbF_6	68.3	12.6	19.1
KBF_4 - NF_4SbF_6	15.3	79.6	5.1
$CsBF_4$ - NF_4SbF_6	85.4	13.3	1.3

(a) A 5 mole % excess of the NF_4^+ salt was used in all runs, except for the $LiBF_4$ - NF_4BiF_6 system, where approximately stoichiometric amounts of starting materials were used.

expected, the solubilities of the alkali metal hexafluoro-antimonates and bismuthates are much higher in the concentrated solutions of the metathetical runs. Furthermore, Table III shows that a cesium salt-based process results in the best product purity. The extremely low yield of NF_4BF_4 for the KBF_4 - NF_4SbF_6 system is caused by KBF_4 being less soluble in HF than $KSbF_6$. Keeping the difference in the stoichiometry of the used starting materials in mind, (see footnote of Table III) the results obtained for the $LiBF_4$ - NF_4SbF_6 and the $LiBF_4$ - NF_4BiF_6 system are roughly comparable.

Oxonium Hexafluorobismuthate

Our interest in the possible existence of $H_3O^+BiF_6^-$ was twofold. The salt has previously been proposed [1] as a potential candidate for the removal of traces of water from HF. Furthermore, its possible formation in wet HF solutions of BiF_5 might interfere with metathetical experiments, or result in undesired by-products, particularly when BiF_6^- salts are prepared from BiF_5 and alkali metal fluorides in HF solution [13].

It was found that, contrary to a previous literature report [13], BiF_5 is quite soluble in anhydrous HF and has a solubility in excess of 300 mg of BiF_5 per g of HF at 22°. The Raman spectrum of this solution (Figure 2, trace A) significantly differs in the deformation region from those of the BiF_6^- anion in HF solution (Figure 2, trace B) and of solid BiF_5 [16, 19], but is not unreasonable for an associated hexacoordinated bismuth fluoride.

On addition of water to this solution a copious white precipitate formed. The formation of this less soluble solid in the presence of small amounts of water could explain the previous report [13] on the low solubility of BiF_5 in supposedly anhydrous HF. The Raman spectrum (Figure 2, trace B) of the HF solution above the white solid showed one polarized (591 cm^{-1}) and two depolarized bands (520 and 220 cm^{-1}), in agreement with our expectations for octahedral BiF_6^-. These frequency values are similar to those observed for the alkali metal BiF_6^- salts in the solid state (see above). The Raman spectrum of the precipitate was also recorded and was similar to that of the liquid phase. These observations show that water addition converts HF dissolved BiF_5 into a BiF_6^- salt.

Further identification of the formed precipitate was achieved by pumping off the HF solvent at -45°. Based on the observed material balance and vibrational spectra, the following reaction occurred

$$H_2O + HF + BiF_5 \longrightarrow H_3O^+BiF_6^-$$

The Raman spectra of the solid product (Figure 2, traces C) showed the presence of the bands characteristic for BiF_6^- (see above) and H_3O^+ [1]. The presence of these ions was further confirmed by infrared spectroscopy at -196° which showed a strong band at 3240 cm^{-1} with a shoulder at 3000 cm^{-1} due to H_3O^+ stretching and a very intense

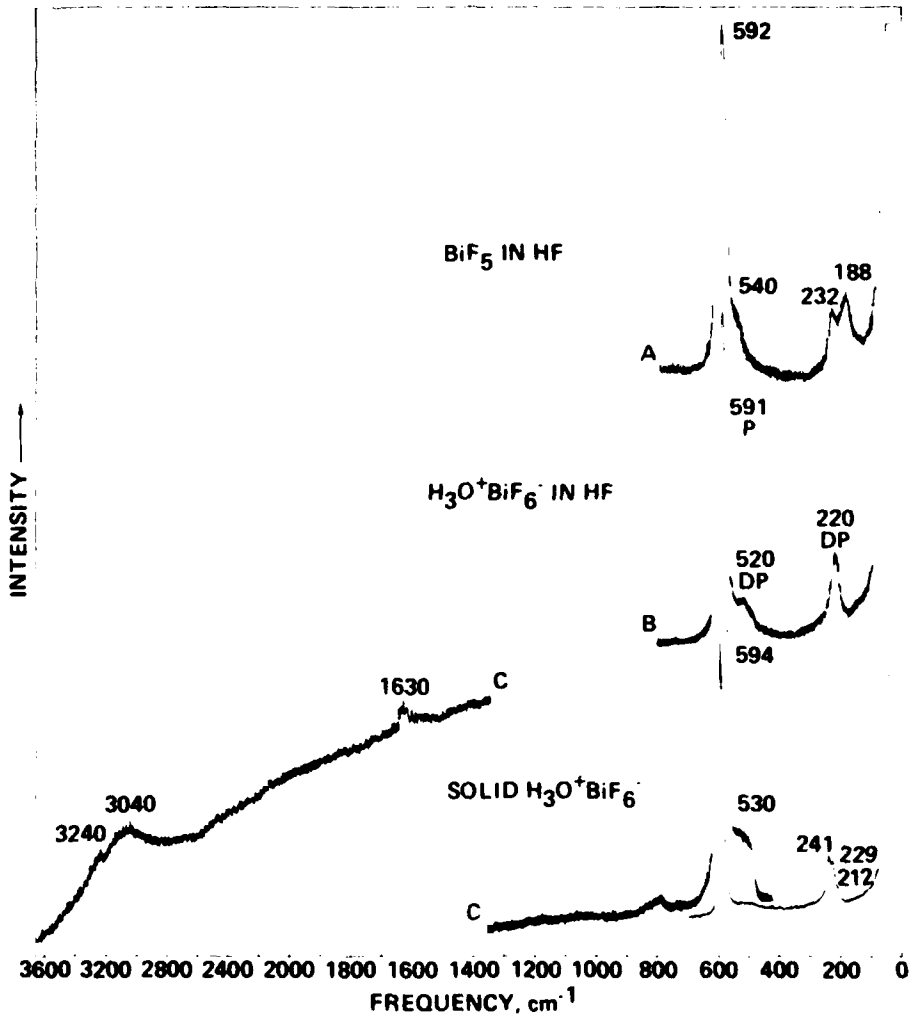

Figure 2. Raman spectra of a 1 molar solution of BiF_5 in HF (trace A), a saturated solution of H_3OBiF_6 in HF (trace B), and of solid H_3OBiF_6 (trace C). All spectra were recorded at room temperature. P and DP indicates polarized and depolarized lines, respectively.

broad band with maxima at 598, 566 and 538 cm^{-1} due to BiF_6^- stretching. The splittings for the BiF_6^- stretching mode is not surprising since at the low temperature rotational motions of the ions in the crystal lattice are frozen out [1] causing symmetry lowering due to strong anion-cation interactions. The same temperature effect was observed for the Raman spectra. At -100°, the 594 cm^{-1} band was observed to split into the following bands: 595 vs, 586 s, 574 mw, 562 w, 555 sh.

An interesting behavior was observed for solid H_3OBiF_6. At ambient temperature, H_3OBiF_6 appears to be stable only under an HF pressure of about 20 torr. When the HF is pumped off, the compound turns instantly dark brown indicating hydrolysis of BiF_5 [9]. When the HF pressure is restored, the solid turns white again. The nature of the decomposition product was established by allowing a sample of H_3OBiF_6 to completely decompose in a dynamic vacuum for 3 days at 35°. The solid residue was found to be mainly BiF_3, as expected from the known [9] hydrolysis of BiF_5. Based on these observations, it appears that H_3OBiF_6 first undergoes a reversible dissociation according to

$$H_3OBiF_6 \rightleftharpoons H_2O + HF + BiF_5$$

followed by the irreversible hydrolysis

$$BiF_5 + H_2O \longrightarrow BiF_3 + 2HF + 1/2O_2$$

with the first step being strongly suppressed by HF.

Although the thermal stability of H_3OBiF_6 appears to be lower than that [1] of H_3OSbF_6, the following reaction cycle might offer a convenient method for drying HF:

$$BiF_5 + H_2O + HF \longrightarrow H_3OBiF_6$$

$$H_3OBiF_6 \longrightarrow BiF_3 + 3HF + 1/2O_2$$

$$\underline{BiF_3 + F_2 \longrightarrow BiF_5}$$

$$H_2O + F_2 \longrightarrow 2HF + 1/2O_2$$

The advantage of this cycle over one using SbF_5 would be that BiF_5 is a nonvolatile solid which is easier to handle. As shown by the above equations, the proposed cycle amounts to a fluorination of water to yield HF and oxygen. Although this objective can also be achieved by a direct treatment of wet HF with high pressure fluorine with agitation [1], the proposed cycle could offer practical advantages. For example, in the proposed cycle the fluorination step could be limited to a relatively small amount of BiF_3 instead of treating the bulk of the HF with a large excess of high pressure fluorine which has to be recovered.

Acknowledgement

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APPENDIX C

CHEMISTRY AND STRUCTURE OF $N_2F_3^+$ SALTS

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Chemistry and Structure of $N_2F_3^+$ Salts

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The novel $N_2F_3^+$ salt $N_2F_3SbF_6$ was prepared from N_2F_4 and SbF_5 in anhydrous HF solution. A metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 in HF produced N_2F_4 and the novel salt $N_2F_3SnF_5$. It was shown that N_2F_4 and BF_3 do not form a stable adduct at temperatures as low as −78 °C. The vibrational and ^{19}F NMR spectra of the $N_2F_3^+$ cation were reexamined. All the experimental data are consistent with a planar structure of symmetry C_s for $N_2F_3^+$. The previously reported vibrational assignments made on the basis of a nonplanar structure of symmetry C_1 are revised for six fundamental frequencies.

Introduction

The first report on the formation of a stable adduct between N_2F_4 and a Lewis acid was published[1] in 1965 by Ruff. He showed[1,2] that SbF_5, when treated with an excess of N_2F_4 in AsF_3 solution, produced, depending on the pressure of N_2F_4, either the 1:2 adduct $N_2F_4 \cdot 2SbF_5$ or the 1:3 adduct $N_2F_4 \cdot 3SbF_5$. On the basis of the observed ^{19}F NMR spectrum and an incomplete infrared spectrum, he assigned to $N_2F_4 \cdot 2SbF_5$ the ionic structure $N_2F_3^+Sb_2F_{11}^-$ with hindered rotation around the N–N bond in $N_2F_3^+$. In 1967, Young and Moy published[3]

the syntheses of adducts between N_2F_4 and AsF_5. At −78 °C and ambient temperature, the AsF_5:N_2F_4 combination ratios were reported to be 2.3 and 1.3 ± 0.2, respectively. In addition to an incomplete infrared spectrum and an unresolved ^{19}F NMR spectrum, the strongest lines of an X-ray powder diffraction pattern were given which was indexed on the basis of a cubic unit cell with a = 10.8 Å. In the same year, Lawless published[4] a better resolved infrared spectrum of $N_2F_3AsF_6$, but no assignments were offered. In 1970, Qureshi and Aubke published[5] a paper dealing with the infrared and Raman spectra of solid $N_2F_3AsF_6$ and $N_2F_3Sb_2F_{11}$. With the exception of the N–N torsional mode, they observed and tentatively assigned all fundamental vibrations of $N_2F_3^+$ proposing a nonplanar structure of symmetry C_1.

Since $N_2F_3^+$ salts are of interest as burning aids in solid propellant NF_3–F_2 gas generator formulations,[6] we have studied (i) the synthesis of $N_2F_3SbF_6$, (ii) the possibility of converting $N_2F_3SbF_6$ into "self-clinkering"[7] $N_2F_3^+$ salts by metathetical reactions,[8] and (iii) the vibrational spectra and structure of the $N_2F_3^+$ cation. The results of this study are summarized in this paper.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3) Monel vacuum line equipped with Teflon-FEP U-traps and diaphragm valves. Pressures were measured with either a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM 56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Arsenic pentafluoride and SbF_5 (Ozark Mahoning), N_2F_4 (Air Products), and BF_3 and SO_2 (Matheson) were purified by fractional condensation prior to use. The BrF_5 (Matheson) was treated with F_2 at 200 °C and then purified by fractional condensation. HF was dried as previously described.[9] The SnF_4 (Ozark Mahoning) was used as received. The preparation of Cs_2SnF_6 has previously been described.[7]

The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgBr or AgCl disks in a Wilks minipellet press. Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-Å exciting line and a Claassen filter[10] for the elimination of plasma lines. Polarization measurements for HF solutions in thin-walled KelF capillaries were carried out by method VIII, as described[10] by Claassen et al. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon FEP sample tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel-filtered copper Kα radiation.

Synthesis of $N_2F_3SbF_6$. A Teflon ampule, containing a Teflon-coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox and attached to the vacuum line. Then 2 mL of anhydrous HF was condensed into the ampule at −78 °C. While the mixture was stirred and warmed to ambient temperature, the system was pressurized with N_2F_4 (~1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4. Periodic cycling to below 0 °C seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40 °C until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4. When the reaction was repeated on a larger scale with 8 mL of HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $N_2F_3SbF_6$ (weight of $N_2F_3SbF_6$ calculated for 74.0 mmol of SbF_5: 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

Synthesis of $N_2F_3AsF_6$. A 30-mL stainless steel cylinder was loaded at −196 °C with 22.8 mmol of AsF_5 and 26.8 mmol of N_2F_4. In a prechilled but empty Dewar, the cylinder was allowed to warm slowly from −196 °C to room temperature. Unreacted N_2F_4 (4.0 mmol) was recovered by pumping at ambient temperature. The weight (6.25 g) of the resulting white solid was in excellent agreement with that (6.25 g) calculated for 22.8 mmol of $N_2F_3AsF_6$. The compound, when prepared in this manner, always was slightly tacky, but hard. It was characterized by ^{19}F NMR and vibrational spectroscopy.

The N_2F_4–BF_3 Systems. Equimolar amounts of N_2F_4 and BF_3, when combined at −78 °C in a Teflon-FEP ampule, did not form a solid. The liquid could be distilled at −78 °C to a colder trap without leaving any solid residue behind.

The N_2F_4–SnF_4 System. A suspension of SnF_4 (4.68 mmol) in 4 mL of liquid HF in a Teflon-FEP ampule was pressurized with N_2F_4 (12.7 mmol) to a pressure of 900 mm. The mixture was stirred for 5 days at room temperature. On the basis of its vibrational spectra and chemical analysis, the white solid residue obtained upon removal of all material volatile at 25 °C did not contain any $N_2F_3^+$.

Synthesis of $N_2F_3SnF_5$. Solid $N_2F_3SbF_6$ (6.48 mmol) and Cs_2SnF_6 (3.24 mmol) were placed in a previously described Teflon-FEP apparatus, and approximately 2 mL of anhydrous HF was added. After the system was stirred and shaken vigorously for 30 min at room temperature, some of the HF was removed under vacuum and the mixture was cooled to −78 °C. The solid and liquid phases were separated by pressure filtration, and the volatile products were removed by pumping at 25 °C for 15 h. The volatile material was separated by fractional condensation and consisted of the HF solvent and N_2F_4 (3.2 mmol). The filtrate residue (0.3 g) was shown by vibrational spectroscopy to contain the $N_2F_3^+$ and $(SnF_5^-)_n$ ions[1-5,7] as the main components, in addition to a small amount of SbF_6^-. The filter cake consisted mainly of $CsSbF_6$ with lesser amounts of $N_2F_3SnF_5$.

Attempts were unsuccessful to suppress N_2F_4 evolution in the above reaction by carrying out the entire metathesis at −78 °C. Again N_2F_4 evolution and $N_2F_3SnF_5$ formation were observed.

Results and Discussion

Synthesis. For the metathetical synthesis of $N_2F_3^+$ salts using the $CsSbF_6$ process,[8] $N_2F_3SbF_6$ was needed as a starting material. Although Ruff had studied[1,2] the interaction of N_2F_4 with SbF_5 in a solvent, such as AsF_3, he had obtained only the polyantimonates $N_2F_3Sb_2F_{11}$ and $N_2F_3Sb_3F_{16}$. We found that, if this reaction is carried out in HF solution using excess N_2F_4 at a pressure of about 1 atm, $N_2F_3SbF_6$ can be obtained in quantitative yield and excellent purity according to

$$N_2F_4 + SbF_5 \xrightarrow[\text{room temp}]{\text{HF soln}} N_2F_3SbF_6$$

Similarly, no difficulty was encountered in preparing a well-defined 1:1 adduct between N_2F_4 and AsF_5. In this case, no solvent was required and the yield was quantitative:

$$N_2F_4 + AsF_5 \xrightarrow{25\ ^\circ C} N_2F_3AsF_6$$

According to a previous report[3] by Young and Moy on the same system, the averaged composition of their adduct was $N_2F_4 \cdot 1.33AsF_5$ and, in the presence of HF as a solvent, the yield was only about 65%.

Boron trifluoride, which is a weaker Lewis acid than SbF_5 and AsF_5, does not form a stable adduct with N_2F_4 at temperatures as low as −78 °C. Our attempts also failed to directly synthesize an $N_2F_3^+$ salt derived from SnF_4 by treatment of a SnF_4–HF suspension with N_2F_4. No N_2F_4 uptake occurred. This lack of reactivity cannot be due to insufficient acid strength of SnF_4 since metathesis in HF yields stable $N_2F_3SnF_5$ (see below). A more plausible explanation is that N_2F_4 is not a strong enough Lewis base to depolymerize SnF_4.

Since the direct synthesis of an adduct between N_2F_4 and SnF_4 was not possible, a metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 was carried out in HF solution. The following reaction occurred:

$$2N_2F_3SbF_6 + Cs_2SnF_6 \xrightarrow[78\ ^\circ C\ \text{filtration}]{\text{HF soln}} 2CsSbF_6\downarrow + N_2F_3SnF_5 + N_2F_4$$

The $N_2F_3SnF_5$ salt is a white solid, stable at room temperature. It is considerably more soluble in HF than $CsSbF_6$, thus making the metathesis possible. Attempts were unsuccessful to prepare $(N_2F_3)_2SnF_6$ by modification of the above reaction

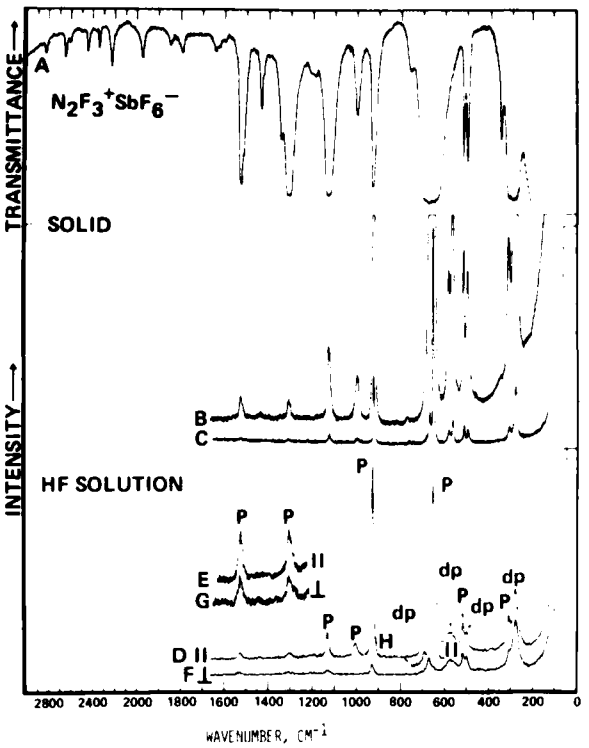


Figure 1. Vibrational spectra of $N_2F_3SbF_6$: trace A, infrared spectrum of the solid as an AgBr disk, the broken line being due to absorption by the window material; traces B and C, Raman spectrum of the solid recorded at two different recorder voltages with spectral slit widths of 3 and 8 cm^{-1}, respectively; traces D–H, Raman spectra of an HF solution recorded at different recorder voltages and spectral slit widths (5 and 8 cm^{-1}) with incident polarization parallel and perpendicular (p and dp stand for polarized and depolarized bands, respectively).

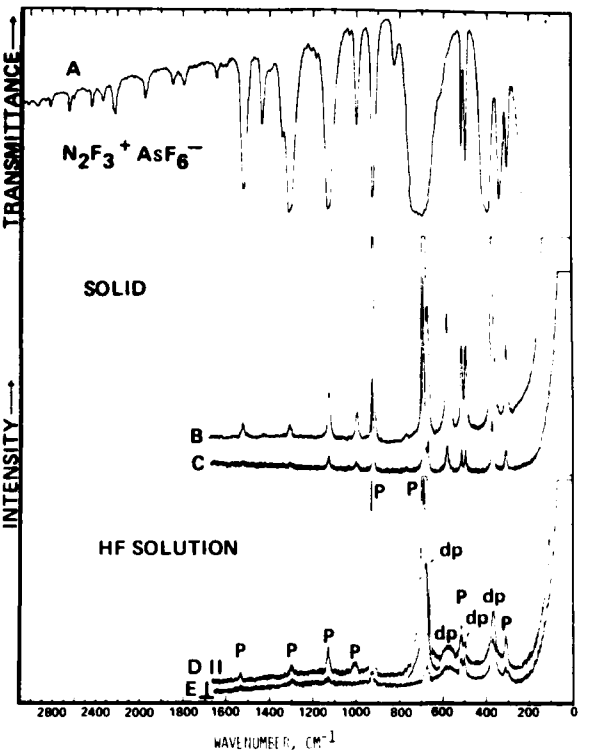
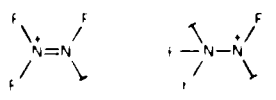


Figure 2. Vibrational spectra of $N_2F_3AsF_6$. For explanation, see caption of Figure 1.

conditions. This was somewhat unexpected in view of the fact that previously no difficulty was encountered in the preparation of the analogous $(NF_4)_2SnF_6$ salt from NF_4SbF_6 and Cs_2SnF_6 under similar reaction conditions.[7] It should be remembered, however, that the favored reaction product from the displacement reaction between NF_4BF_4 and SnF_4 in HF was NF_4SnF_5 and not $(NF_4)_2SnF_6$.[7] These results indicate that the reaction chemistry of SnF_4 and its anions in HF is rather complex and hard to predict without exact knowledge of the corresponding solvation and lattice energies of the possible products.

Vibrational Spectra. Figures 1–3 show the vibrational spectra of $N_2F_3SbF_6$, $N_2F_3AsF_6$, and $N_2F_3SnF_5$, respectively. The observed frequencies are listed in Tables I and II. The vibrational spectra of SbF_6^-,[5,6,11,12] AsF_6^-,[5,11,13,14] and $(SnF_5^-)_n$[7] are well-known and can be assigned without difficulty (see Tables I and II). The remaining bands should be due to the $N_2F_3^+$ cation.

The $N_2F_3^+$ cation could possess either a planar structure of symmetry C_s (I) or a nonplanar structure of symmetry C_1



I (C_s) II (C_1)

caused by significant contributions from resonance structure II. The assignments previously made[5] by Qureshi and Aubke for $N_2F_3^+$ were based on symmetry C_1, although structure II is energetically considerably less favorable than I (one nitrogen possesses only six valence electrons) and is in poor agreement

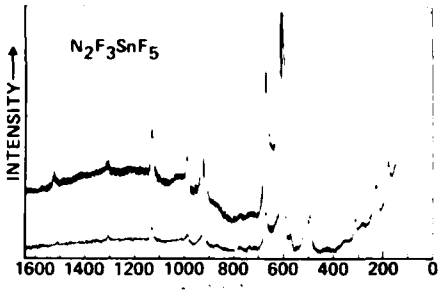


Figure 3. Raman spectrum of solid $N_2F_3SnF_5$ recorded at two different recorder voltages.

with the published NMR data[1,2] which show hindered rotation around the N–N bond up to at least 120 °C. Symmetry C_1 had previously been chosen[4] because the highest Raman frequency observed for either solid $N_2F_3AsF_6$ or $N_2F_3Sb_2F_{11}$ occurred at about 1310 cm^{-1}. Since this frequency is considerably lower than expected[15,16] for an N=N bond, significant contributions from II were assumed.[5]

As can be seen from Figures 1–3, the highest Raman band observed for all three $N_2F_3^+$ salts occurs at about 1520 cm^{-1}, thus confirming the original assignment[1–3] of the strong 1520-cm^{-1} infrared band to the N=N stretching mode and eliminating the basis for Qureshi and Aubke's reassignment.[5] The previous failure to observe the 1520-cm^{-1} Raman band can be explained by its relatively low intensity and the low signal to noise ratio in the reported spectrum.[5]

Having established the identity of the N=N stretching mode, we can now proceed to test if the rest of the $N_2F_3^+$ spectrum is consistent with symmetry C_s. For $N_2F_3^+$ of C_s symmetry a total of nine fundamental vibrations is expected of which six belong to species A′ and three belong to A″. An approximate description of these nine modes is given in Table

Table I. Vibrational Spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$

assignments for $N_2F_3^+$ in point group C_s	obsd freq, cm^{-1}, and rel intens[a]						assignments for MF_6^- in point group O_h
	$N_2F_3SbF_6$			$N_2F_3AsF_6$			
	solid		HF soln	solid		HF soln	
	IR	Raman	Raman	IR	Raman	Raman	
$\nu_1 + \nu_2$ (A′) = 2829	2825 vw			2820 vw			
$\nu_1 + \nu_3$ (A′) = 2649	2647 vw			2643 vw			
$2\nu_2$ (A′) = 2614	2608 vvw			2605 vvw			
$\nu_1 + \nu_4$ (A′) = 2447	2443 vw			2440 vw			
$\nu_2 + 2\nu_5$ (A′) = 2339	2343 vw			2340 vw			
$\nu_2 + \nu_4$ (A′) = 2232	2227 w			2223 w			
$\nu_3 + \nu_4$ (A′) = 2052	2050 sh						
$\nu_2 + \nu_7$ (A″) = 1978	1976 w			1970 w			
$2\nu_4$ (A′) = 1850	1850 vw			1846 vw			
$\nu_3 + \nu_7$ (A″) = 1798	1796 vw			1795 vw			
$\nu_3 + \nu_5$ (A′) = 1643	1642 vw			1639 vw			
$\nu_2 + \nu_6$ (A′) = 1617	1619 sh			1617 vvw			
$\nu_4 + \nu_7$ (A″) = 1596	1599 vvw			1596 vvw			
ν_1 (A′)	1522 s	1522 (0.1)	1522 (0.1) p	1519 s	1520 (0.2)	1524 (0.2) p	
$\nu_3 + \nu_6$ (A′) = 1437	1436 m	1424 (0+)	1435 (0+)	1432 *m*	1430 (0+)		
				1390 vw			$\nu_1 + \nu_3$ (F_{1u})
$2\nu_7$ (A′) = 1342	1343 m			1340 m			
ν_2 (A′)	1310 vs	1307 (0.1)	1306 (0.1) p	1307 vs	1305 (0.2)	1300 (0.2) p	
$\nu_5 + 2\nu_6$ (A′) = 1204	1210 vw			1206 vw			$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
$\nu_5 + \nu_7$ (A″) = 1187	1189 vw			1186 vw			
ν_3 (A′)	1127 vs	1124 (0.4)	1127 (0.6) p	1128 vw	1127 (0.6)	1128 (0.7) p	
$2\nu_5$ (A′) = 1032	1033 vvw			1032 vvw			
$2\nu_8$ (A′) = 994	998 m	997 (0.2)	1000 (0.25) p	996 m	997 (0.3)	1001 (0.3) p	
ν_4 (A′)	925 s	924 (3.2)	927 (6.1) p	923 s	925 (4.7)	929 (5.9) p	
	755 mw			826 mw			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
	670 vs			699 vs			ν_3 (F_{1u})
ν_7 (A″)		670 (0.9)	671 (0.8) dp		671 (0.9)	671 (0.8) dp	
		656 (10)	655 (10 *p*		690 (10)	689 (10) p	ν_1 (A_{1g})
				620 sh			$\nu_5 + \nu_6$ ($A_{1u} + E_u + F_{1u} + F_{2u}$)
		582 (0.4) } 566 (1.1) }	575 (0.4) dp		581 (1.3)	575 (0.4) dp	ν_2 (E_g)
ν_5 (A′)	515 ms	514 (0.8)	518 (1.0) p	515 ms	516 (1.2)	516 (0.9) p	
ν_8 (A″)	497 ms	496 (0.5)	499 (0.6) dp	496 ms	497 (1.1)	498 (0.5) dp	
ν_9 (A″)	345 m	348 (0+)		343 ms			
ν_6 (A′)		310 (0.5)	310 (0.6) p		310 (0.9)	310 (1.0) p	
	290 vs			392 s			ν_4 (F_{1u})
		280 (2.4)	280 (2.3) dp		374 (3.6)	371 (2.0) dp	ν_5 (F_{2g})

[a] Uncorrected Raman intensities.

Table II. Vibrational Spectra of Solid $N_2F_3SnF_5$

obsd freq, cm^{-1}, and rel intens		assignment	
IR	Raman	$N_2F_3^+$ (C_s)	$(SnF_5^-)_n$
1518 s	1519 (0.1)	ν_1 (A′)	
1428 *m*		$\nu_3 + \nu_6$ (A′)	
1341 m		$2\nu_7$ (A′)	
1304 vs	1304 (0.1)	ν_2 (A′)	
1126 vs	1127 (0.5)	ν_3 (A′)	
986 m	988 (0.4)	$2\nu_8$ (A′)	
921 vs	921 (3.9)	ν_4 (A′)	
	670 (1.1)	ν_7 (A′)	
635 } 610 } s, br	604 (10)		str modes
	572 (0.3)		
	512 (2)	ν_5 (A′)	
490–450 m, br	492 (1)	ν_8 (A″)	bridge str
	310 (0.8)	ν_6 (A′)	
	228 (1.3)		def modes
	179 (1.1)		

Table III. Fundamental Frequencies (cm^{-1}) of $N_2F_3^+$ and Their Assignment in Point Group C_s

freq	assignment	approx description of mode
1522	A′ ν_1	N=N str
1307	ν_2	asym NF_2 str
1127	ν_3	NF′ str
925	ν_4	sym NF_2 str
516	ν_5	δ(sym NF_2) in plane
310	ν_6	δ(FNNF_2) in plane
671	A″ ν_7	δ(asym FNNF_2) out of plane
497	ν_8	δ(sym FNNF_2) out of plane
344	ν_9	N=N torsion

III. All nine modes should be infrared and Raman active, with a possible exception being the torsional mode ν_9 which is expected to be of very low Raman intensity. The three A″ modes should result in depolarized Raman bands.

As can be seen from Table III, three NF stretching modes are expected all belonging to species A′ and occurring in the frequency range 900–1300 cm^{-1}. There are three very intense infrared bands in this region (see Figures 1 and 2), all of which have Raman counterparts. Of the three predicted NF stretching modes, the symmetric NF_2 stretch (ν_4) is expected to have the highest Raman intensity and the lowest depolarization ratio and, therefore, is assigned to the band at about 925 cm^{-1}. The reverse should hold true for the antisymmetric NF_2 stretching mode ν_2 which, therefore, is assigned to the band at about 1310 cm^{-1}. This leaves the assignment of the band at about 1127 cm^{-1} to the unique NF stretching mode ν_3, the frequency of which is similar to that of the NF stretch in N_2F^+.[17]

For the assignment of the five deformation modes, the following five frequencies are available: 671, 516, 497, 344, and 310 cm^{-1}. Of these, the 516- and 310-cm^{-1} bands are clearly polarized in the Raman spectra and therefore must represent the two remaining A′ modes. By comparison with

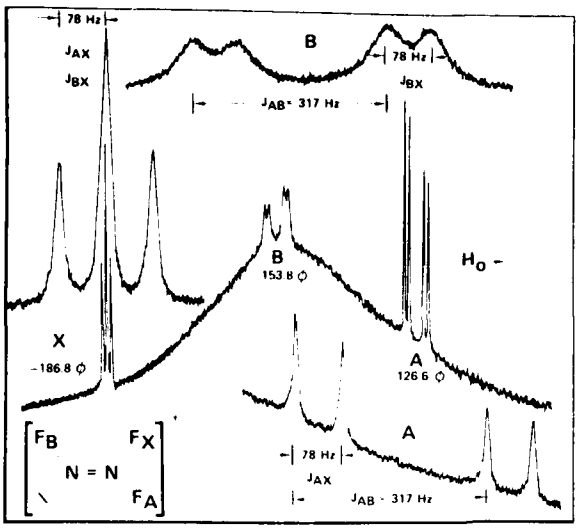


Figure 4. ^{19}F NMR spectrum of $N_2F_3AsF_6$ in BrF_5 solution, recorded at -78 °C and 84.6 MHz using $CFCl_3$ as external standard. The very broad background signal is due to rapidly exchanging BrF_5 and AsF_6^-. The inserts show the A, B, and X signals, all recorded with tenfold scale expansion, but different recorder gain settings.

the known frequencies of the NF_2[18] and CF_2[19] radicals, the 516-cm^{-1} band is assigned to the NF_2 scissoring mode ν_5, leaving the 310-cm^{-1} band for the unique FNN in-plane deformation mode ν_6.

Of the remaining three fundamental frequencies, the 671- and 497-cm^{-1} ones exhibit reasonably intense depolarized Raman bands, whereas the 344-cm^{-1} one has been observed only in one Raman spectrum (Figure 1, trace B) as an extremely weak band. In the infrared spectra, the 344-cm^{-1} fundamental is of medium intensity. These intensity relations indentify the 344-cm^{-1} band as the N=N torsional mode. Of the two remaining frequencies, the 671-cm^{-1} fundamental is assigned to the antisymmetic and the 497-cm^{-1} fundamental to the symmetric $FNNF_2$ out-of-plane deformation. This assignment is based on that[20] of the related C_2F_4 molecule. Numerous combination bands were observed in the infrared spectra. Their assignment is given in Table I.

In summary, the vibrational spectra of the $N_2F_3^+$ ion are entirely consistent with our predictions for a planar model of symmetry C_s. All nine fundamentals were observed, with six of them being polarized and two of them being depolarized in the Raman spectra. As expected, the torsional mode is of very low Raman intensity. The double-bond character of the NN bond in $N_2F_3^+$ is confirmed by the high frequencies of the NN stretching and the torsional mode.

NMR Spectra. The ^{19}F NMR spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ were recorded at 84.6 MHz in SO_2, BrF_5, SbF_5, and HF solution. The HF solvent was acidified with either AsF_5 or SbF_5 to suppress exchange between the solvent and the cation.[20,22] In HF, BrF_5, and SbF_5 solutions, exchange between the anions and the solvent was observed; however, in SO_2 solution separate signals were observed for AsF_6^- at ϕ 57 and SbF_6^- at ϕ 111 with the appropriate area ratios.

For $N_2F_3^+$, a typical ABX pattern with an area ratio of 1:1:1 was observed at about ϕ 127, 154, and 187, respectively. The chemical shifts of these signals exhibited only little solvent and temperature dependence. Even at 150 °C (SbF_5 solution), no averaging of the NF resonances was noticeable, indicating strongly hindered rotation about the N–N axis, as expected for a N=N. These findings are in excellent agreement with the previous report by Ruff for $N_2F_3Sb_2F_{11}$ in SO_2 solution and the melt.

Our low-temperature spectra (-70 to -90 °C) in either BrF_5 (see Figure 4) or acidified HF solutions were much better resolved than those obtainable for the SO_2 solution and thus permitted a more accurate determination of the three coupling constants. The A signal consisted of a sharp doublet of doublets with J_{AB} = 317 Hz, J_{AX} = 78 Hz, and a line width of about 8 Hz. The B signal was again a doublet of doublets with J_{AB} = 317 HZ and $J_{BX} \approx$ 78 Hz, but with significantly broader lines (line width of about 60 Hz). The X signal was a sharp 1:2:1 (J = 78 Hz) triplet indicating very similar values of J_{AX} and J_{BX}. Our observed coupling constants significantly differ from those (J_{AB} = 379 Hz, J_{AX} = 81 Hz, J_{BX} = 45 Hz) previously reported[2] for a poorly resolved spectrum.

Assignment of ABX to the three fluorines in $N_2F_3^+$ can be made based on the following arguments. The two nitrogen atoms in $N_2F_3^+$ are not equivalent. The one possessing only one fluorine ligand is centered in an electrically less symmetric field thus making ^{14}N quadrupole relaxation more effective and causing line broadening. Consequently, the broadened B signal is assigned to the unique fluorine. Since for the related FN=NF, CF_2=NF, and substituted fluoroethylenes the cis coupling constants were found to be always significantly smaller than the trans ones,[23] A (J_{AB} = 317 Hz) should be trans and X (J_{BX} = 78 Hz) should be cis with respect to B. The resulting structure is shown in Figure 4. The observed coupling constants are similar to those observed for cis FN=NF (J = 99 Hz) and trans FN=NF (J = 322 Hz).[23]

X-ray Powder Data. The X-ray powder patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ are given as supplementary material. Young and Moy have reported[3] the three strongest lines for $N_2F_3AsF_6$ and stated that the pattern can be indexed for a cubic unit cell with a = 10.8 Å. Although our data confirm the three previously reported lines,[3] our observed pattern cannot be indexed based on the previously given unit-cell dimensions. In view of the nonspherical geometry of $N_2F_3^+$, a relatively small cubic unit cell would be very surprising for $N_2F_3AsF_6$.

Acknowledgment. We are indebted to Drs. L. R. Grant and W. W. Wilson for helpful discussions and to Mr. R. D. Wilson for experimental help. This work was supported in part by the Office of Naval Research and the U.S. Army Research Office.

Registry No. $N_2F_3SbF_6$, 67328-70-5; $N_2F_3SnF_5$, 67328-71-6; $N_2F_3AsF_6$, 12254-91-0; N_2F_4, 10036-47-2; SbF_5, 7783-70-2.

Supplementary Material Available: Table IV, listing the observed X-ray powder diffraction patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ (1 page). Ordering information is given on any current masthead page.

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ESR SPECTRA OF THE $^{14}NF_3^+$ AND $^{15}NF_3^+$ RADICAL CATIONS

Electron Spin Resonance Spectra of the $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$ Radical Cations

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The ESR spectra of the $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$ radical cations were observed over the temperature range 15–340 K. The radical cations were generated either by γ irradiation of NF_4^+ salts or by low-temperature UV photolysis of NF_3–F_2–Lewis acid mixtures. For $NF_3^{+\cdot}$, two different types of spectra were observed. At the lower temperatures, a highly anisotropic spectrum was obtained which is attributed to a rigid radical. At the higher temperatures, a more isotropic spectrum was observed which is attributed to $NF_3^{+\cdot}$ of axial symmetry. An analysis of the observed spectra was carried out and was supported by computer simulations and the observed ^{15}N isotopic data. It was found that the previously reported value of the isotropic fluorine hyperfine splitting is incorrect. The resulting spin density distributions indicate that $NF_3^{+\cdot}$ is pyramidal but that within the isoelectronic series $BF_3^{-\cdot}$, CF_3, $NF_3^{+\cdot}$ the planarity of the radicals increases from $BF_3^{-\cdot}$ toward $NF_3^{+\cdot}$.

Introduction

Radicals and radical ions formed from first-row elements have been the subject of numerous studies. These species provide experimental data by which molecular orbital models can be tested and also define limits within which the properties of isoelectronic species can be predicted. Electron spin resonance (ESR) provides a useful technique for studying the structure of these radicals[1] since the spin distribution in s and p orbitals can be determined from hyperfine splittings (hfs) and limits can often be set on the energies of excited states through the *g* factors.[1,2]

This study was prompted by the following observations: (i) During a recent study[3] of the synthesis of NF_4^+ salts, ESR spectra were obtained which were substantially different from those previously reported.[4] The radicals exhibiting these spectra were stable up to 250 K, depending upon the particular anion. The ESR spectra recorded at these higher temperatures could not be reconciled with the parameters previously given by Mishra et al.[4] (ii) On the basis of the known isotropic fluorine hyperfine splittings (a_F(iso)) of isoelectronic $BF_3^{-\cdot}$ (17.8 mT)[5] and CF_3 (14.35 mT),[6–10] the value of 16.7 mT previously reported[4] of $NF_3^{+\cdot}$ appeared to be much too high if a monotonic trend in the values for a_F(iso) is assumed for the isoelectronic series. Since the values of the hyperfine splittings can be used to determine the structure of these radicals, a reexamination of the previously given[4] analysis of the ESR spectra seemed necessary. For this purpose, it was also found necessary to study the isotopically labeled $^{15}NF_3^{+\cdot}$ to permit unambiguous assignment of the nitrogen hfs.

In this paper we report the ESR spectra of $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$, including a study of their temperature dependencies and a revised analysis of the hyperfine splittings.

Experimental Section

Synthesis of $^{15}NF_4^+$ Salts. The low-temperature UV photolysis experiments of NF_3–F_2–Lewis acid mixtures were carried out in quartz containers as previously described.[3] The $^{15}NF_3$ used in some of these experiments was prepared by glow discharge of $^{15}N_2$ (99% ^{15}N, Stohler Isotope Chemicals) and F_2 (Rocketdyne) mixtures according to the method of Maya.[11] The samples of NF_4BF_4 and NF_4AsF_6 used for the ^{60}Co γ-irradiation experiments were prepared by low-temperature UV photolysis in a quartz reactor using a previously described[3] method. The samples of NF_4^+ antimonates were prepared by heating mixtures of NF_3, F_2, and SbF_5 at elevated pressures in a Monel cylinder.[12] These salts were recrystallized from anhydrous HF to remove residual Monel salt impurities.

γ Irradiation. NF_4^+ salts were transferred in a dry nitrogen atmosphere into 4-mm o.d. quartz tubes (J. T. Scanlon Co., Solvang, Calif.) which were flame-sealed under vacuum. Typically, samples of 100 mg of $^{14}NF_4^+$ salts were used while only 15 mg samples of $^{15}NF_4^+$ salts were available. Samples were exposed to ^{60}Co γ irradiation at 77 K, using a flux rate of 4×10^5 R h^{-1}. Samples of the $^{14}NF_4^+$ salts were exposed between 15 and 24 h, while the sample of the $^{15}NF_4^+$ salt was exposed for 40 h. Samples were annealed in dry ice (195 K) prior to recording their ESR signals. The NF_4^+ signal intensity did not decrease even when the samples were stored at 195 K for several months.

UV Experiments. The conditions used for the UV photolyses have previously been described.[3]

ESR Spectra. ESR spectra were recorded using a computer-controlled ESR spectrometer previously described.[14] The spectrometer operated at 9.303 GHz with a TE_{104} rectangular dual cavity and an ITD-3-110 (Air Products) Helitran temperature controller. A 15-in. magnet was used with the spectrometer. Signal averaging combined with programs for smoothing spectra and removal of background signals was used to record weak spectra. Intense spectra were recorded using standard dual cavity techniques. The magnetic field standard was Mn^{2+}.[15] Values of the magnetic parameters were $a_{^{55}Mn} = 8.673 \pm 0.003$ mT (1 T = 10^4 Oe) and $g = 2.000\,95 \pm 0.000\,05$.[16] Field positions were computed to third order. Spectra were recorded between 15 and 340 K.

Simulations of ESR Spectra. Simulations of the ESR spectra of powders were carried out using a program developed by White and Belford based on the method of Pilbrow and Winfield[17] and modified by Chasteen.[18] The program computes second-order shifts of one nucleus and permits the hyperfine axis of that nucleus to be nonparallel to the remainder of the hyperfine axes. It also allows anisotropic line widths to be used in the calculation. The program was further modified in our laboratory to include second-order splittings from one equivalent set of nuclei.

Results

ESR Spectra. During a recent ESR study[3] of the UV photolysis of mixtures of NF_3, F_2, and BF_3 or AsF_5, spectra similar to that shown in Figure 1a were observed at ca. 77 K. However, as shown in Figure 1 of ref 3, these spectra were very poorly resolved. These spectra, which were attributed to a immobile $NF_3^{+\cdot}$ radical cation in a matrix, are expected to exhibit unique features (singularities) which correspond to the orientation of the threefold symmetry axis of the radical along directions parallel and perpendicular to the applied magnetic field. However, only the parallel component of the spectrum is clearly identifiable.

Upon warming of the UV-photolyzed mixture, the spectra began to change. The thermal stability of the observed ESR signals strongly depended upon the Lewis acid used. For AsF_5 the ESR signal became more intense about 130 K and appeared to be more isotropic. At 180 K, the signal started to lose intensity, and it decayed rapidly at 230 K. This loss of signal intensity can be attributed to the disappearance of the condensed AsF_5 phase. However, a relatively weak residual signal remained above 230 K which can be attributed to $NF_3^{+\cdot}$ trapped in the solid NF_4AsF_6 formed during the UV photolysis. For the more volatile BF_3, the change from the anisotropic low-temperature spectrum to the more isotropic higher temperature one occurred at about 117 K. At 140 K, the

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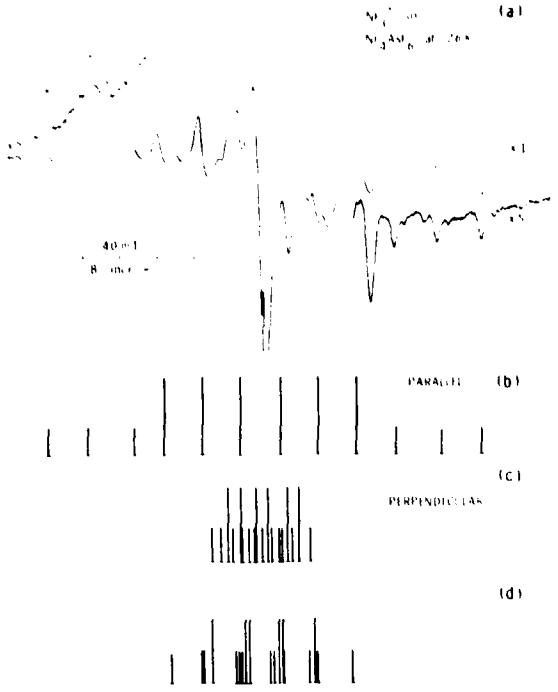

Figure 1. (a) ESR spectrum of $^{14}NF_3^{+}\cdot$ at 26 K in NF_4AsF_6 γ irradiated at 77 K after annealing at 195 K. (b) Stick plots of the line positions to first order, assuming parallel F-atom tensors with the C_3 axis of the radical aligned parallel to the applied field. (c) Stick plot to second order of the line positions of the radical with its C_3 axis *perpendicular to the applied field (our analysis).* (d) Stick plot to second order under conditions of (c) using the previously reported assignment. See discussion of (c) and (d) in text.

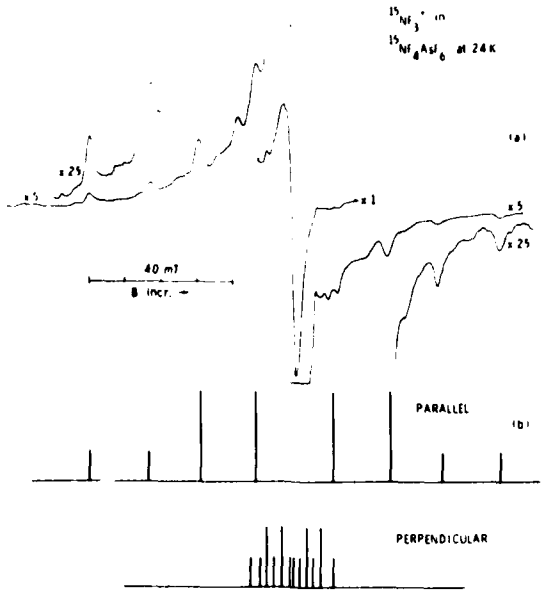

Figure 2. (a) ESR spectrum of $^{15}NF_3^{+}\cdot$ at 24 K in $^{15}NF_4AsF_6$ γ irradiated at 77 K after annealing at 195 K. (b) Stick plots of the line positions for the C_3 axis of the radical aligned parallel and perpendicular to the applied field, assuming parallel fluorine hfs tensors.

$NF_3^{+}\cdot$ signal was completely lost. Although the more isotropic spectra observed for the NF_3, F_2, AsF_5 and NF_3, F_2, BF_3 systems exhibited broad lines, it became evident that they could not be interpreted in terms of the parameters previously assigned to $NF_3^{+}\cdot$.

In order to resolve these disparities, the temperature dependence of the ESR spectra of the γ-irradiated salts of NF_4^{+} was investigated. Salts used in this study were NF_4BF_4, NF_4AsF_6, NF_4SbF_6, and $NF_4SbF_6{\cdot}0.8SbF_5$, all of which gave similar spectra after γ irradiation at 77 K, followed by annealing at 195 K in solid CO_2. Contrary to Mishra,[4] no problem was encountered in generating $NF_3^{+}\cdot$ by γ irradiation of NF_4BF_4. Prior to annealing, residual signals were observed on either side of the $NF_3^{+}\cdot$ resonance, in addition to an intense sharp line at $g = 2$. The origin of these signals, which may have been due to the anion,[4] was not investigated. The annealed samples exhibited different spectra at high and low temperatures. The low-temperature spectrum, observed between 10 and 140 K, was similar to that previously attributed to $NF_3^{+}\cdot$,[4] and is shown in Figure 1 for irradiated NF_4AsF_6 at 26 K. Other salts gave similar spectra, except that the lines exhibited a shoulder to the high field side of the main resonance. The line width of the spectrum increased slightly with longer irradiation times but was independent of temperature. Reducing the amount of $NF_3^{+}\cdot$ by warming the sample resulted in a narrower line. These observations suggest that dipolar interactions occurred between nearby defect sites. There is one difference between our spectra and that observed by Mishra et al.,[4] even in the more dilute solutions, we were unable to resolve some of the features which were attributed to the alignment of the C_3 axis of the radical perpendicular to the magnetic field. We did, however, observe shoulders at these positions.

As the temperature of the arsenate and antimonate salts is increased to the range 140 and 235 K, the low-temperature spectrum collapses and then forms a sharper one with a narrower span. This spectrum is independent of temperature between 240 and 340 K, where decomposition begins, and is shown in Figure 3 for irradiated NF_4AsF_6 at 240 K. The lifetime of the species at room temperature is about 2 weeks but decreases to about 10 min at 340 K. Similar spectra were observed for the irradiated borate salts between about 270 and 320 K.

In order to be certain that the spectra reported here are due to $NF_3^{+}\cdot$, isotopically pure $^{15}NF_4AsF_6$ and $^{15}NF_4BF_4$ were prepared. The signal observed for the irradiated salts exhibited the same temperature dependence as those obtained for $^{14}NF_4^{+}$ salts. However, since only ca. 15 mg of $^{15}NF_4^{+}$ salts was prepared, longer irradiation times had to be used resulting in slightly broadened lines. The low-temperature spectrum of $^{15}NF_3^{+}\cdot$ in $^{15}NF_4AsF_6$ is shown in Figure 2, where the ^{14}N triplets are replaced by ^{15}N doublets. The high-temperature $^{15}NF_3^{+}\cdot$ spectrum is shown in Figure 4 and is analogous to the high-temperature $^{14}NF_3^{+}\cdot$ spectrum.

Discussion

Low-Temperature Spectra of $^{14}NF_3^{+}\cdot$. Several unusual features become apparent upon close inspection of the $NF_3^{+}\cdot$ spectra at low temperatures. Most significantly, the distinct, intense features of the spectra must be assigned to the radical with its threefold symmetry (C_3) axis aligned parallel to the applied magnetic field. Generally, however, the most intense features of the spectra of axially symmetric radicals in powders are assigned to the orientation in which the symmetry axis is perpendicular to the applied field.[18-20] Since no such features are observed here, it is clear that this spectrum cannot be treated in the conventional manner used for axial or nearly axial symmetry.

A second feature is that the positions of the lines in the spectrum that correspond to the $\parallel$ orientation do not fall into the positions calculated from the hyperfine splittings (hfs)

Table I. Hyperfine Splittings[a] of $^{14}NF_3^+$ and $^{15}NF_3^+$ at High and Low Temperatures

	$^{14}NF_3^+$		$^{15}NF_3^+$	
	26 K	240 K	24 K	240 K
$a_F(\parallel)$	30.8[c]	2.00 ± 0.25	30.6[c]	2.40 ± 0.25
$a_F(\perp)$	(−)3.3[c]	12.48 ± 0.05	(−)3.8[c]	11.97 ± 0.05
$a_N(\parallel)$	11.49 ± 0.20	8.70 ± 0.25	−16.08 ± 0.20	12.20 ± 0.25[c]
$a_N(\perp)$	7.8 ± 0.5	9.36 ± 0.05	10.6 ± 1.0	13.03 ± 0.05[c]
a_F(iso)	8.1	8.99 ± 0.14	7.7	8.78 ± 0.14
a_N(iso)	9.0	9.14 ± 0.14	12.4	12.75 ± 0.14
$g(\parallel)$	2.003 ± 0.002	2.0073 ± 0.0010	2.003 ± 0.002	2.0079 ± 0.0012
$g(\perp)$	2.006 ± 0.002	2.0040 ± 0.0007	2.005 ± 0.002	2.0047 ± 0.0007
g(iso)	2.005 ± 0.002	2.0051 ± 0.0007	2.005 ± 0.002	2.0058 ± 0.0009

[a] Hyperfine splittings are in mT (1 mT = 10 Oe). [b] The sign of the ^{14}N hfs is assumed to be positive; thus ^{15}N hfs are negative by virtue of their nuclear moments. [c] These are effective values based on supposed axial symmetry for individual tensors; $a_F(z) = 30.8$ mT and $a_F(x) = a_F(y) \sim 3.3$ mT (see text).

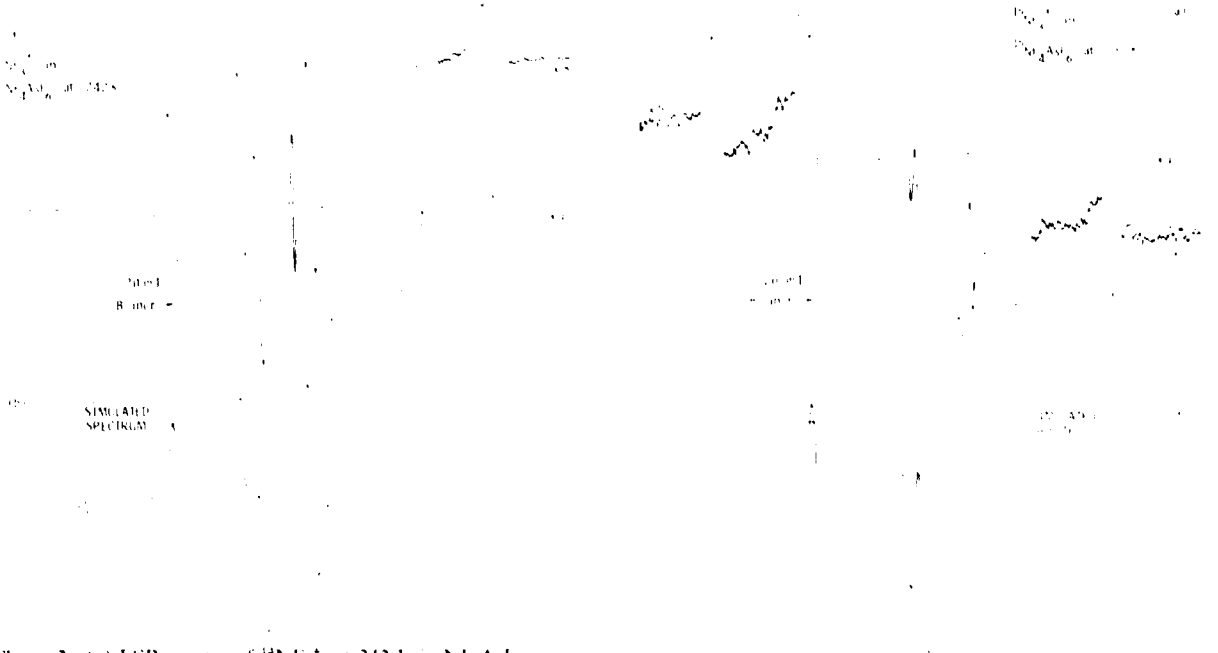

Figure 3. (a) ESR spectra of $^{14}NF_3^+$· at 242 K in NF_4AsF_6 γ-irradiated at 77 K. (b) Computer simulation of spectrum assuming axial symmetry and the parameters given in Table I.

which are given in Table I. These values are calculated from the extrema of the spectrum. For a system which exhibits a large hfs with axial symmetry, the field positions in which the unique axis is parallel to the magnetic field, $H_{I,M_I}(\parallel)$, is given by eq 1 to second order,[21] where $g(\parallel)$, $g(\perp)$, $a(\parallel)$, and $a(\perp)$

$$H_{I,M_I}(\parallel) = H_0(\parallel) - a(\parallel)M_I - \frac{a(\perp)^2[g(\perp)/g(\parallel)]^2}{2[H_0(\parallel) - a(\parallel)M_I]}[I(I+1) - M_I^2] \quad (1)$$

are the parallel and perpendicular g factors and hfs, respectively. $H_0(\parallel)$ is given by $h\nu/g(\parallel)\mu_B$. I is the total nuclear spin, and M_I is the component of spin parallel to the magnetic field. The analogous equation for $H_{I,M}(\perp)$ is given by eq 2.[21]

$$H_{I,M_I}(\perp) = H_0(\perp) - a(\perp)M_I - \frac{a(\perp)^2 + a(\parallel)^2[g(\parallel)/g(\perp)]^2}{4[H_0(\perp) - a(\perp)M_I]}[I(I+1) - M_I^2] \quad (2)$$

where $H_0(\perp)$ is given by $h\nu/g(\perp)\mu_B$. Field positions are plotted on the same field axis under the spectrum in Figure 1b, for the molecule oriented $\parallel$ and $\perp$ to the field. Second-order shifts are only significant for NF_3^+· when the field is $\perp$ to the C_3 axis of the radical. Note that for the $\parallel$ orientation, while the lines corresponding to $M_I(F) = +^3/_2$ and $-^3/_2$ agree with the calculated positions, the lines corresponding to $M_I(F) = +^1/_2$ and $-^1/_2$ are shifted away from the center of the spectrum.

Figure 4. (a) ESR spectra of $^{15}NF_3^+$· at 235 K in $^{15}NF_4AsF_6$ γ-irradiated at 77 K. (b) Computer simulation of spectrum assuming axial symmetry and parameters given in Table I.

A final complication in the interpretation of this spectrum is that there are several extra lines present which cannot be explained in the conventional analysis assuming axial symmetry. Similar features were observed in spectra of CF_3· which were explained[9,10] by the fact that, while the hyperfine tensors of each of the fluorine atoms are equivalent, they are not mutually parallel. This causes the axial component of the tensor to be at an angle of 18° with respect to the C_3 symmetry axis.[9] As a result, singularities in the spectrum appear which correspond to orientations of the radical with respect to the applied field which are other than parallel or perpendicular.

In the spectrum of CF_3·, there are sets of lines which correspond to either the parallel or the perpendicular orientation. However, these do not occur in the positions expected from the values of the hfs. Because $a_I(\parallel) > a_I(\perp)$, the lines $|M_I(F)| = \frac{3}{2}$ which correspond to parallel alignment are shifted closer to the center of the spectrum, while those of

$|M_I(F)| = {}^1/_2$ are shifted away from the center. Shifts in opposite directions occur for the lines which correspond to the perpendicular orientation. The effective value, $a_F(\|)$, is then given by eq 3, where $a_x = a_y$ and a_z are the principal values of the hyperfine tensor

$$a_F^2(\|) = a_z^2 \cos^2 \alpha + a_x^2 \sin^2 \alpha \qquad (3)$$

The spectrum of $NF_3^+\cdot$ is more complicated because of the added anisotropy of the ^{14}N hfs. Here the nitrogen hyperfine tensor will determine the positions of the singularities of the spectrum. As a result, the treatment given by Maruani et al.[9,10] for $CF_3\cdot$ needs to be modified. We report here, effective values for the hyperfine tensor, determined from the extrema of the spectra. In units of mT, $a_F(\|) = 30.8$, $a_F(\perp) = 3.3$, $a_N(\|) = 11.49$, and $a_N(\perp) = 7.8$. In contrast, Mishra et al.[4] report $a_F(\|) = 30.0$, $a_F(\perp) = 10.0$, $a_N(\|) = 11.5$, and $a_N(\perp) = 9.0$. The stick plot representing this analysis is shown in Figure 1b,c for the parallel and perpendicular orientations, respectively. The analysis of the parallel orientation is in agreement with the previous[4] assignment; however, there is substantial difference between our analysis of the perpendicular orientation and the previous one,[4] shown in Figure 1d. The analysis of the perpendicular components depends upon which features are selected. Since these features are buried within the spectrum and since extra lines appear, this assignment is indeed difficult. However, because of the large value of $a_F(\|)$, there are downfield shifts of 1.5 mT due to second-order effects. Therefore, the features corresponding to the perpendicular orientation are those which are asymmetric with respect to the center of the spectrum, after allowing for the second-order splittings of the $|M_I(F)| = {}^1/_2$ lines. Furthermore, the features that we have selected are consistent with the analyses of high-temperature spectra as well as those derived from the $^{15}NF_3^+\cdot$ spectra.

Low-Temperature Spectra of $^{15}NF_3^+\cdot$. In order to confirm the analysis of the $^{14}NF_3^+\cdot$ spectra, samples of isotopically pure $^{15}NF_4^+$ salts were prepared. Since only 15 mg of sample was available, long irradiation times were used to get a sufficiently strong signal. This resulted in some line broadening. Nevertheless, because the spectra are less complicated, some features of the $\perp$ orientation can be observed. The result of the analysis is given in Table I. Within experimental error, the fluorine hfs are equivalent for $^{14}NF_3^+\cdot$ and $^{15}NF_3^+\cdot$, while their nitrogen hfs are in the ratio of their nuclear magnetogyric ratios (1.403). The observed spectrum and a stick-plot of the analysis are shown in Figure 2. Note also that the spectrum exhibits anomalies similar to those discussed for $^{14}NF_3^+\cdot$.

High-Temperature Spectra of $^{14}NF_3^+\cdot$. The high-temperature spectrum of $^{14}NF_3^+\cdot$ shown in Figure 3 can be interpreted in terms of an axially symmetric radical containing three nuclei of $I = {}^1/_2$ and one nucleus of $I = 1$. A unique feature of this spectrum is that the hfs for the parallel orientation are smaller than those of the $\perp$ orientation. However, as discussed earlier, the features representing the $\perp$ orientation are considerably stronger than those of the $\|$ orientation. As a result, the features of the parallel orientation in the middle of the spectra are masked, and they can only be determined by computer simulation. For $^{14}NF_3^+\cdot$ in NF_4AsF_6, the spectrum is interpreted in terms of a nitrogen nucleus ($I = 1$) and three equivalent fluorine nuclei ($I = {}^1/_2$). The hyperfine splittings are, in mT, $a_N(\perp) = 9.36$, $a_N(\|) = 8.70$, $a_F(\perp) = 12.48$, and $a_F(\|) = 2.00$. These values are independent of temperature between 235 and 340 K.

High-Temperature Spectra of $^{15}NF_3^+\cdot$. In order to confirm the assignment of the $^{14}NF_3^+\cdot$ spectra, spectra of a γ-irradiated sample of $^{15}NF_4AsF_6$ were obtained (Figure 4). These spectra can be analyzed in terms of one ^{15}N atom ($I = {}^1/_2$) and three equivalent ^{19}F atoms ($I = {}^1/_2$). The hyperfine splittings are given in Table I. The $^{15}NF_3^+\cdot$-containing samples exhibited the same thermal stability as the $^{14}NF_3^+\cdot$-containing samples described above.

Comparison of High- and Low-Temperature Spectra. The g factors and hyperfine splittings of the different $NF_3^+\cdot$ ESR spectra are given in Table I. That they are all due to $NF_3^+\cdot$ is established by the following observations: spectra of the irradiated ^{14}N and ^{15}N salts contain nuclei of the correct spins and numbers; fluorine atom hfs of $^{14}NF_3^+\cdot$ and $^{15}NF_3^+\cdot$ are equal at high and low temperatures, respectively, while the respective N-atom hfs are in the correct ratio of their nuclear moments; high-temperature spectra reversibly change into the low-temperature spectra, which are less intense; computed values of the isotropic hfs are the same in high- and low-temperature spectra, provided that the sign of $a_F(\perp)$ at low temperature is taken as negative.

The reason for the difference between the high-temperature and the low-temperature spectra is probably due to temperature-dependent rotation of $NF_3^+\cdot$ about a single axis. Spectra of $CF_3\cdot$ in a 1:30 CF_3I/Kr matrix change from one characteristic of a stationary radical to one characteristic of a freely rotating radical, as the temperature is increased from 4.2 to 35 K.[10] Examples in which similar changes occur between 77 and 300 K include $NH_3^+\cdot$ and $ND_3^+\cdot$ in their respective ammonium perchlorates[22] and $PF_5\cdot$ in KPF_6.[23,24] The averaging processes for $NH_3^+\cdot$ and $ND_3^+\cdot$,[22] as well as $PF_5\cdot$,[24] were attributed to rotations of these radical ions.

As the temperature of the $NF_3^+\cdot$-containing samples is increased, the spectra change between two different anisotropies. At low temperatures, the spectra are indicative of motionless $NF_3^+\cdot$, while at high temperatures, the spectra are indicative of uniaxial rotation. Most likely, this rotation occurs about an axis close to that of its minimum moment of inertia and is probably accompanied by some libration. Preliminary X-ray studies[26] on NF_4BF_4 show that the lattice is tetragonal, which may provide a preferential direction for rotation of the smaller $NF_3^+\cdot$ cation. Since this radical should be in its minimum energy configuration, significant deviations from the energetically favored pyramidal structure are extremely unlikely. Also, there are no phase changes of the lattice between 100 K and room temperature as indicated by Raman spectroscopy.[25] Inversion of the radical about the nitrogen would be expected to result in more nearly complete averaging.

Supporting evidence for rotation of $NF_3^+\cdot$ is provided by the fact that the $a_F(\perp)$ values observed for $^{14}NF_3^+\cdot$ and $^{15}NF_3^+\cdot$ are not identical. Since $NF_3^+\cdot$ has a pyramidal structure (see below), the moments of inertia of $^{14}NF_3^+\cdot$ and $^{15}NF_3^+\cdot$ must be different. This causes their rotational axes to be different, resulting in different $a_F(\perp)$ values.

UV-photolyzed mixtures of NF_3, BF_3, and Lewis acid at low temperatures exhibited spectra which were similar to that of Figure 1, except that the lines were broader. The line width increased slightly with longer photolysis, while the intensity increased. The higher temperature spectra (see for example Figure 5) can be interpreted in terms of the hyperfine parameters of the $NF_3^+\cdot$ spectra observed for the γ-irradiated salts (see Figure 3), although the line widths are quite different. For the photolyzed samples, the transition between the low and higher temperature spectra occurred at much lower temperatures than the γ-irradiated salts and the thermal stability of the radical depended upon the volatility of the Lewis acid used (see Results section). This suggests that these radicals are associated with solid AsF_5 or BF_3. The weaker residual signals observed after complete evaporation of the NF_3–F_5 Lewis acid condensed phases are similar to those in the γ-irradiated $NF_4^+\cdot$ salts. This suggests that they are due to $NF_3^+\cdot$ trapped in small amounts of $NF_4^+\cdot$ salts formed during the photolysis.

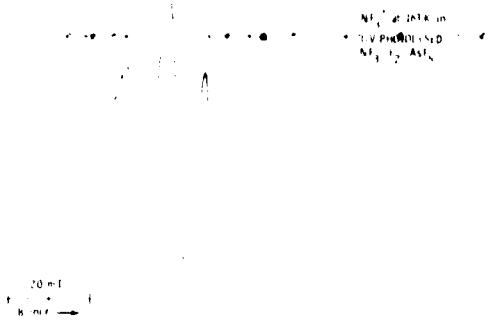

Figure 5. ESR spectrum of the $NF_3^{+\cdot}$ radial at 163 K produced by UV photolysis of a mixture of NF_3, F_2, AsF_5 (1:4:1) at 77 K. Comparison with Figure 1a shows that the six intense lines of the spectra are broadened into four overlapping lines, with the wings not resolved.

Table II. Comparison of Hyperfine Couplings of Radicals XF_3 Used in Table III

	$^{14}NF_3^{+\cdot}$ [a]	$^{12}CF_3^{\cdot}$ and $^{13}CF_3^{\cdot}$	$^{11}BF_3^{-\cdot}$ [b]	$^{14}NF_2O^{\cdot}$ [c]
$a_X(\perp)$	7.8[d]	24.7[f]		
$a_X(\parallel)$	11.49[d]	31.8[f]		
$a_F(\perp)$	0.3.3[d]	8.4[g]		
$a_F(\parallel)$	30.8[d]	26.4[g]		
a_F(iso)	8.98[e]	14.25[h]	17.8	14.34
a_X(iso)	9.14[e]	27.15[h]	15.3	9.39
g(iso)	2.0051[e]	2.0031[h]	2.0021	2.0058

[a] This work. [b] Reference 5. [c] References 27 and 28. [d] Taken from low-temperature spectra. [e] Taken from high-temperature spectra. [f] Reference 29. [g] Reference 9. [h] Reference 6.

Table III. Spin Densities on the Central Atom and Fluorine Atoms of $NF_3^{+\cdot}$ Compared to Those of Related Radicals

radical	ρ_X^s(X)	ρ_X^p(X)	ρ_F^s	g(iso)
$BF_3^{-\cdot}$	0.212		0.0104	2.0021
$CF_3^{\cdot}$	0.245	0.717	0.0084	2.0029
$NF_3^{+\cdot}$	0.166	0.687	0.0053	2.0051
$NF_2O^{\cdot}$	0.170		0.0084	2.0058
$NF_2^{\cdot}$	0.030	0.956	0.0052	2.0044

[a] Spin densities calculated from the data in Table II, assuming that atomic isotropic hyperfine couplings a in mT are 72.1 for B, 111.0 for C, 55.0 for N, and 17100 for F, and the atomic anisotropic couplings b are 3.24 for C and 1.71 for N. (See ref 30.)

Structures of $NF_3^{+\cdot}$. ESR data for $NF_3^{+\cdot}$ and isoelectronic species are compared in Table II. Since the tensors of the fluorine hfs need not be exactly axially symmetric, we averaged those in the CF_3 radical[9] to yield an effective value to be compared with that of $NF_3^{+\cdot}$. The spin densities on the s and p orbitals, ρ_i^s and ρ_i^p, respectively, of the central atom, given in Table III, were calculated by eq 4 and 5, where a_i and b_i

$$\rho_i^s = a_i(\text{iso}) / a_i^\circ \tag{4}$$

$$\rho_i^p = (a_i(\parallel) - a_i(\text{iso})) / 2b_i^\circ \tag{5}$$

are the isotropic and anisotropic hfs of an electron in the s and p orbitals of atom i, and a_i(iso) is the calculated isotropic hfs. For $BF_3^{-\cdot}$, no experimental anisotropic hfs were available, and values calculated from ref 31 had to be used.

The values of ρ_X^s for $NF_3^{+\cdot}$ and $NF_2O^{\cdot}$ are nearly the same, as expected from the isoelectronic character of the F^- and O^- substituents. Although the ρ^s values for the series $NF_3^{+\cdot}$, $CF_3^{\cdot}$, and $BF_3^{-\cdot}$ do not follow a monotonic trend, without a measured value for the anistropic boron hfs, the hybridization cannot be accurately determined. The value of ρ^p/ρ^s for $CF_3^{\cdot}$ is 2.9, while that of $NF_3^{+\cdot}$ is 4.1. This suggests that the free electron in $NF_3^{+\cdot}$ has more p character than that in $CF_3^{\cdot}$. This in turn suggests that the hybridization of the XF bonds in $CF_3^{\cdot}$ is nearly sp^3 but that in $NF_3^{+\cdot}$ is between sp^3 and sp^2. This in turn indicates that $NF_3^{+\cdot}$ is more planar than $CF_3^{\cdot}$ in contrast to the conclusion of Mishra et al.[4] This is further supported by the fact that the observed anisotropy in the fluorine hfs is greater for $NF_3^{+\cdot}$ than for $CF_3^{\cdot}$. Recent theoretical calculations[31] based on the isotropic hfs of $BF_3^{-\cdot}$, $CF_3^{\cdot}$, and $NF_3^{+\cdot}$ also indicate that the planarity increases from $BF_3^{-\cdot}$ toward $NF_3^{+\cdot}$.

The same conclusions are reached if the values of a_i° and b_i° reported by Hurd and Coodin[32] are used. These values are approximately 15% larger than those used here, so that smaller spin densities are computed. Although these absolute values appear more realistic, they leave the ratios of ρ^p/ρ^s unchanged.

The spin densities of $NF_3^{+\cdot}$ and $NF_2^{\cdot}$ are also compared in Table III. The spin density distribution for $NF_2^{\cdot}$ is calculated from the ESR data of Kasai and Whipple,[33] and the data are consistent with the isotropic data of Farmer et al.[35] Values in mT are $a_N(\parallel) = 4.9$, $a_N(\perp) = 0.0$, $a_F(\parallel) = 21.2$, and $a_F(\perp) = 16.9$. In $NF_2^{\cdot}$, the unpaired electron is primarily in a p orbital so that there is no delocalization of the unpaired electron into the orbital of the lone pair on nitrogen. Thus, the structure of this radical is surprisingly different from that of $NF_3^{+\cdot}$.

Work is underway to analyze, in detail, the hyperfine splittings of the $NF_3^{+\cdot}$ radical and determine the angle α between the nitrogen and fluorine hyperfine tensors. In the $CF_3^{\cdot}$ radical, α was found to be 17.8°.[9,10] Edlund et al.[35] reported that the direction of the hfs was not perpendicular to the C–F bond, but at an angle of 54° to it. A precise analysis of the low-temperature spectrum of $NF_3^{+\cdot}$ may substantiate the above conclusions. Since the $NF_3^{+\cdot}$ radical is slightly more planar, α for $NF_3^{+\cdot}$ may be different from that of $CF_3^{\cdot}$.

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Contribution from the Rockwell International Science Center, Thousand Oaks, California 91360, and Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304

APPENDIX E

FORMATION AND DECOMPOSITION MECHANISM OF NF_4^+ SALTS

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Contribution from the Rocketdyne Division, Rockwell International, Canoga Park, California 91304, and the Science Center, Rockwell International, Thousand Oaks, California 91360

Formation and Decomposition Mechanism of NF_4^+ Salts

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The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total-pressure measurements. It was found that the rates, previously reported by Solomon and co-workers for NF_4AsF_6, significantly differ from those of the present investigation, although both studies result in a $^1/_2$ reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies: $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}. The suppression of the decomposition rates by NF_3, F_2, and BF_3 or AsF_5 was measured. A critical evaluation of all experimental data available on the NF_4^+ salt formation and decomposition suggests the following reversible reaction mechanism: $F_2 \rightleftarrows 2\dot{F}$; $\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$; $\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$; $\dot{N}F_3^+AsF_6^- + \dot{F} \cdot \cdot NF_4^+AsF_6^-$. A Born–Haber cycle calculated for NF_4BF_4 shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF_4SbF_6 at 250 °C was also studied.

Introduction

The formation and decomposition reactions of NF_4^+ salts are of significant theoretical and practical interest. From a theoretical point of view, the question arises as to whether $\dot{N}F_4$ or NF_5 is produced as an unstable intermediate. This would be highly unusual because second-row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decom-

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position mechanism is necessary in order to improve on existing synthetic methods.

Several mechanisms have previously been postulated for the formation of NF_4^+ salts. In 1966, Christe and co-workers suggested in their original reports[1,2] on the synthesis of NF_4AsF_6 by low-temperature glow discharge that either NF_3^+ or F^+ (or F_2^+) is generated in the discharge. These radical cations could then react with either F_2 or NF_3 to yield NF_4^+. In 1972, Solomon and co-workers reported[3] the results from a kinetic study of the thermal decomposition of NF_4AsF_6 in Monel. Based on total pressure measurements, their conclusion was that the decomposition involved the equilibrium dissociation step

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$$

followed by irreversible decomposition of the unstable NF_5

$$NF_5 \rightarrow NF_3 + F_2$$

The latter step was taken to be a $^3/_2$-order reaction. From the temperature dependence of the kinetic constants, a value of 41 kcal mol^{-1} was obtained for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_5. In 1973, Christe and co-workers proposed[4] an alternate mechanism for the formation of NF_4^+ salts. This mechanism accounted for the fact that NF_4^+ salts can be synthesized by UV photolysis. It involved the steps

$$F_2 \rightarrow 2\dot{F}$$

$$\dot{F} + AsF_5 \rightarrow \dot{A}sF_6$$

$$\dot{A}sF_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6$$

$$\dot{N}F_3^+AsF_6 + \dot{F} \rightarrow NF_4^+AsF_6$$

Part of this mechanism was later experimentally confirmed by ESR studies[5-7] which showed that the $\dot{N}F_3^+$ radical cation is indeed formed as an intermediate in both the low-temperature UV photosynthesis and the γ-irradiation-induced decomposition of NF_4^+ salts.

Since the observation of $\dot{N}F_3^+$ as an intermediate[5-7] is incompatible with the mechanism proposed[3] by Solomon and since at elevated temperatures metal reactors rapidly absorb F_2–Lewis acid mixtures, a reinvestigation of the thermal decomposition of NF_4AsF_6 in an inert sapphire reactor was undertaken. In particular, a more detailed investigation of the suppression effects of NF_3, F_2, and AsF_5 was expected to yield valuable information. Furthermore, no quantitative data had previously been available on the decomposition rates of NF_4BF_4 and the formation rates of NF_4SbF_6.

Experimental Section

Thermal Decomposition Studies. The samples of NF_4BF_4[8] and NF_4AsF_6[8,9] were prepared as previously described and showed no detectable impurities. All decomposition experiments were carried out in a sapphire reactor (Tyco Co.). The reactor was connected by a Swagelok compression fitting, containing a Teflon front ferrule, to a stainless steel valve and a pressure transducer (Validyne, Model DP7, 0–1000 mm ± 0.5%), the output of which was recorded on a strip chart. The reactor had a volume of 38.7 mL and was heated by immersion into a constant-temperature (±0.05 °C) circulating oil bath. The reactor was passivated at 250 °C with F_2, BF_3, or F_2–AsF_5 mixtures until the pressure remained constant over a period of several days, and weighed amounts of NF_4^+ salts were added in the dry nitrogen atmosphere of a glovebox. After immersion of the reactor into the hot oil bath, the reactor was evacuated, and the pressure change was monitored as a function of time. Control experiments were carried out at the beginning and end of each series of measurements to ascertain that the rates had not significantly changed during each series. The composition of the gaseous decomposition products was shown by chemical analysis, infrared spectroscopy, and gas chromatography to be 1:1:1 mixtures of NF_3, F_2, and the corresponding Lewis acid. For the curve fitting of the kinetic data the method of linear least squares was used with the listed uncertainties being 2σ of the calculated slope.

Formation of NF_4SbF_6. Because of the high corrosivity of high-pressure NF_3–F_2–SbF_5 mixtures at elevated temperatures, the NF_3–F_2–SbF_5 reaction system could not be monitored directly with a pressure transducer or gage. Consequently, nine identical passivated 95-mL Monel cylinders were each loaded with 50 mmol of SbF_5 and a twofold excess of NF_3 and F_2 was added. The cylinders were simultaneously placed into an oven preheated to 250 °C and were removed separately from the oven after certain time intervals. After the cylinders were cooled, all material volatile at 25 °C was pumped off, and the amount of NF_4^+ salt formed was determined by the observed weight increase and spectroscopic analyses.

Results and Discussion

Thermal Decomposition of NF_4BF_4 and NF_4AsF_6. The thermal decomposition of NF_4BF_4 and NF_4AsF_6 in a constant-volume reactor was studied by total-pressure measurements over a temperature range of about 35 °C for each compound. Since screening experiments had shown that even well-passivated nickel or Monel reactors rapidly reacted with mixtures of hot F_2 and BF_3 or AsF_5, a sapphire reactor was used. This reactor was found to be completely inert toward these gas mixtures over extended time periods. Furthermore, it was found that the decomposition rates increased with increasing sample size. However, the rates did not increase linearly with the sample size because the increased pressure enhances the suppression of the rates (see below). In order to minimize the effect of changes in the sample size during a given series of experiments, we used the largest feasible samples and the smallest available reactor volume. In this manner, only a small percentage of the sample was decomposed in a given series of experiments. The first and the last experiment of each series were carried out under identical conditions and showed that the change in rate due to the small, but inevitable, sample-size change was indeed negligible.

The results of our measurements on NF_4BF_4 and NF_4AsF_6 are summarized in Tables I and II. In agreement with the previous report[3] on the thermal decomposition of NF_4AsF_6, smooth decomposition curves were obtained. The decomposition rates steadily decreased with increasing pressure in the reactor and the initial rates were restored upon evacuation of the reactor, indicating that the decomposition products suppress the decomposition rates. This was confirmed by studying the influence of different gases on the decomposition rates of NF_4BF_4 and of NF_4AsF_6. The addition of He did not noticeably influence the rates, whereas F_2 and NF_3 resulted in a weak suppression. However, the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 resulted in strong rate suppressions (see Tables I and II).

For all decomposition experiments, plots of $P^{3/2}$ vs. time resulted in straight lines (see Figures 1 and 2) indicating a $^3/_2$ reaction order. The resulting global kinetic constants are given in Table III. Arrhenius plots of these constants resulted in straight lines (see Figure 3) and in the global decomposition activation energies $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}, the latter value being in good agreement with that of 41 kcal mol^{-1} previously reported.[3]

The fact that the small mole fraction ranges of sample decomposition studied in these experiments were truly representative for the overall decomposition rates was established by following the decomposition of small samples at somewhat higher temperatures over almost the entire mole fraction (α) range. A typical decomposition curve obtained for NF_4BF_4 at 253 °C (see Figure 4) does not exhibit any sigmoid character, and the $P^{3/2}$ vs. time plot is linear for about the first 25% of α.

Although the results previously reported[3] for the decomposition of NF_4AsF_6 in Monel resulted in a linear $P^{3/2}$ vs. time plot, the reported rates were higher than ours by a factor of

Table I. Thermal Decomposition of NF_4BF_4[a] in a Sapphire Reactor[b]

	pressure change, mmHg										
				190.8 °C							
time, h	182.2 °C	188.9 °C	190.8 °C	He (500)[c]	F_2 (500)[c]	NF_3 (500)[c]	BF_3 (500)[c]	197.4 °C	204 °C	213.3 °C	215 °C
0	0	0	0	0	0	0	0	0	0	0	0
1	28	40	45	44	38	38	5	64	91	160	180
2	42	66	74	73	64	64	11	103	142	261	285
3	55	86	97	98	84	87	16	134	191	341	367
4	66.5	102	116	117	102	105	21	161	228	409	440
5	77	117	135	136	122	122	26	186	266	468	509
6	86.5	132	152	153	139	138	31	208	300	522	572
7	96	146	168	169	155	152	35	230	336	579	633
8	104	159	183		169	166	39	250		628	689
9	112	171	197		182	180	43	269		675	741
10	120.5	182	210		195	192	47	288		721	791
12	135	204	236		218	217	56	324		806	891
14	149	225	260		238	239	65	355		895	980
16	162	247	280		258	263	73	390			
18		267	300		277		82				
20					295		91				

[a] Sample size 2.65 g. [b] Reactor volume 38.7 mL. [c] The values given in parentheses indicate the pressure (in mmHg) of the added gas at the beginning of each experiment.

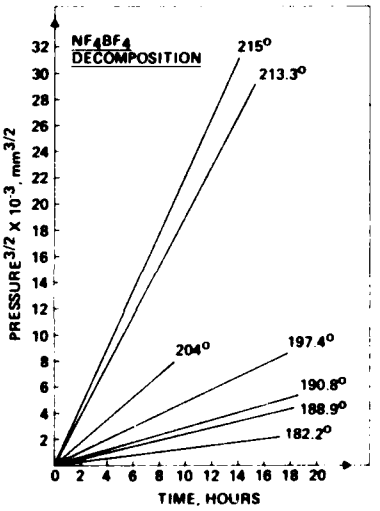


Figure 1. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 2.65 g of NF_4BF_4 at different temperatures (°C).

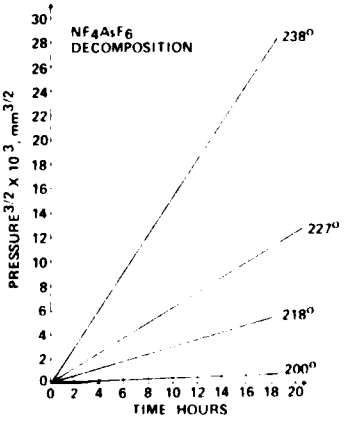


Figure 2. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 1.86 g of NF_4AsF_6 at different temperatures (°C).

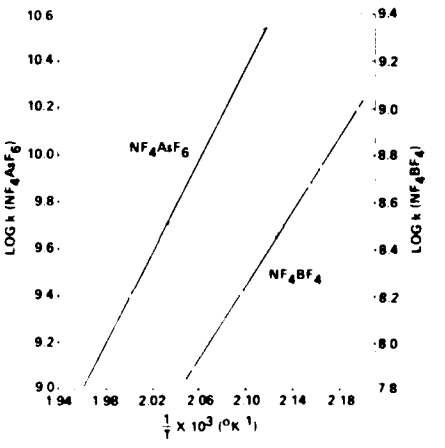


Figure 3. Arrhenius plots for NF_4BF_4 and NF_4AsF_6.

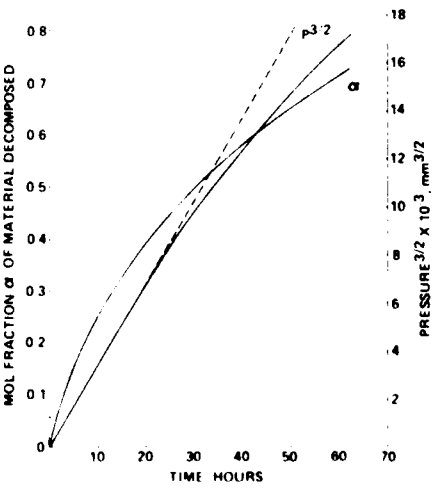


Figure 4. Decomposition curves for 75 mg of NF_4BF_4 at 253 °C. The solid lines are the observed data and the broken line represents the ideal straight line for the $P^{3/2}$ vs. t plot.

about 7. Unfortunately the sample size and the exact reactor volume used in ref 3 were not given. However, the estimated reactor volume (100-cm³ Monel cylinder + Wallace-Tierman FA 145-780 gage) and the reported method of the NF_4AsF_6 synthesis suggest that the previously used sample weight to reactor volume ratios were almost certainly significantly

Table II. Thermal Decomposition of NF_4AsF_6[a] in a Sapphire Reactor[b]

	pressure change, mmHg								
					238 °C				
time, h	200 °C	218 °C	227 °C	238 °C	He (736)[c]	F_2 (197)[c]	NF_3 (567)[c]	AsF_5 (247)[c]	AsF_5 (724)[c]
0	0	0	0	0	0	0	0	0	0
1	2.6	9.9	16	27	28	25	21	5	4
2	4.0	16.0	25	44	45	42	34	8.5	7
3	5.2	20.8	33	58	59	55	44	12	9
4	6.2	25.3	40	71	73	68	54	16.5	11
5	7.2	29.4	46.5	83	85	79	63	20	12
6	8.3	32.2	52.5	93.5	95	90	72	24	13
7	9.2	36.6	57	103.5	105	101	81	28	14
8	10.0	40.0	62	113	115	110	90	32	15.5
9	10.8	43.0	67.5	123	124	120	98	35	17
10	11.6	46.0	72.5	132	133	129	106	38	18
12	13.2	51.4	82	149	151	145	122	45	21
14	14.7	56.6	91	165	166	161	140	52	23
16	16.1	61.4	99.5	181	181	176	160	59	25
18	17.4	66.2	107	197.5	196	190	176	65	
20			115.5	214	213	205	192	72	
25			134				226		
30							252		

[a] Sample size 1.86 g. [b] Reactor volume 38.7 mL. [c] The values given in parentheses indicate the pressure (mmHg) of the added gas at the beginning of each experiment.

Table III. Global Kinetic Constants[a] for the Thermal Decomposition of NF_4BF_4 and NF_4AsF_6

NF_4BF_4		NF_4AsF_6	
temp, °C	10^9k	temp, °C	$10^{10}k$
182.2	0.96 ± 0.01	200	0.284 ± 0.002
188.9	1.74 ± 0.02	218	1.99 ± 0.03
190.8	2.11 ± 0.04	227	4.00 ± 0.02
197.4	3.39 ± 0.05	238	9.69 ± 0.10
204	6.08 ± 0.08	238 (He (736))	9.62 ± 0.08
213.3	12.79 ± 0.22		
215	14.68 ± 0.18	238 (F_2 (197))	9.22 ± 0.05
190.8 (He (500))	2.29 ± 0.03		
		238 (NF_3 (567))	8.60 ± 0.16
190.8 (F_2 (500))	1.86 ± 0.04		
		238 (AsF_5 (247))	1.94 ± 0.12
190.8 (NF_3 (500))	1.92 ± 0.02		
		238 (AsF_5 (724))	0.48 ± 0.08
190.8 (BF_3 (500))	0.314 ± 0.02		

[a] Units $mol^{-2}\ L^2\ s^{-1}$; error limits 2σ.

smaller than those of our experiments. This should have resulted in rates lower than ours. The only possible explanations for the previously reported[3] higher rates are absorption of the suppressing AsF_5 by Monel and/or inaccurate temperature control (heating of the cylinder in a tube furnace).

A large discrepancy of $\sim 10^6$ exists between the previously reported[3] results and our kinetic constants (see Table III). Most of this discrepancy ($\sim 10^4$) appears to be computational.

Furthermore, the previously reported[3] data for the suppression by AsF_5 are inconsistent. Whereas the experimental data in Tables 6 and 7 of ref 3 show strong rate suppression by AsF_5, the kinetic constants given in Table 8 of ref 3 imply *only mild suppression by AsF_5. The previously reported[3] strong* rate suppression by NF_3 could not be confirmed by the present study. Our data (see Table III) show that NF_3 is only a weak suppressor, comparable to F_2, and that AsF_5 or BF_3 is the only strong suppressor. This is an important observation, because the alleged[3] strong suppression by NF_3 had caused us to propose in a previous publication[4] a mechanism for the formation of NF_4AsF_6 involving the incorrect (see below) steps $F + AsF_5 \rightarrow AsF_6$ and $AsF_6 + NF_3 \rightarrow NF_3^+AsF_6^-$.

Thermal Synthesis of NF_4SbF_6. Whereas the thermal synthesis of NF_4AsF_6 proceeds at too slow a rate for practical kinetic measurements, the rate of formation of NF_4SbF_6 is sufficiently fast. However, SbF_5 tends to form polyantimonates such as $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$,[9,11] with SbF_5, which makes a kinetic evaluation of any experimental data very difficult. In view of the importance of the thermal synthesis of NF_4SbF_6 (this compound serves as a starting material for the metathetical syntheses of most other NF_4^+ salts[11-15]) and because of the complete absence of data on its formation rate, nine reactions were carried at 250 °C and at a pressure of

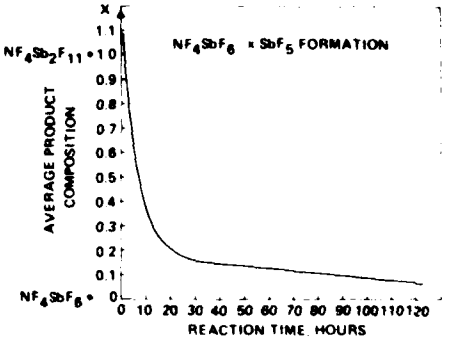


Figure 5. Formation rate of $NF_4SbF_6 \cdot xSbF_5$ from NF_3, F_2, and SbF_5 at 250 °C.

Table IV. Conversion of $NF_3 + F_2 + SbF_5$ to NF_4SbF_6 at 250 °C[a]

reacn time, h	prod compn, $NF_4^+SbF_6^- \cdot xSbF_5$, x	conversn of SbF_5 to NF_4SbF_6, mol %
1	1.08	48.1
2	0.89	52.9
3	0.78	56.2
6	0.59	62.9
12	0.34	74.6
24	0.17	85.5
50	0.13	88.5
85	0.106	90.4
120	0.064	94.0

[a] Mole ratios of starting materials NF_3:F_2:SbF_5 = 2:2:1. Starting pressure 110 atm, residual pressure calculated for 100% conversion to NF_4SbF_6 44 atm. The Monel cylinders (95-mL volume) were placed horizontally in the oven, preheated to 250 °C. One hour was required until the cylinders reached 250 °C. This point was taken as zero reaction time.

about 110 atm to determine its formation rate. The results are summarized in Table IV and Figure 5 and show that at this temperature the initial formation rate of NF_4^+ salts is surprisingly rapid. The subsequent slow-down of the reaction is probably caused by a lowering of the SbF_5 partial pressure in the system due to the formation of polyantimonate anions. Their thermal dissociation equilibria to SbF_6^- and SbF_5 will then control the SbF_5 pressure in the system and become the rate-limiting steps.

Reaction Mechanism. As pointed out in the Introduction, the formation and decomposition mechanism of NF_4^+ salts is of great interest because it appears to involve an unusual hypervalent species such as NF_4, NF_5, AsF_6, or BF_4. The following experimental data are known, and the correct mechanism must be compatible with all of these conditions.

(1) Certain NF_4^+ salts, such as NF_4SbF_6 and NF_4AsF_6, can, depending upon the system pressure, be either formed or decomposed at the same temperature.[5,9-11] This implies pressure-dependent equilibria and reversibility of the formation and decomposition reactions.

(2) ESR measurements have shown[7,8] that the NF_3^+ radical cation is a crucial intermediate in both the low-temperature UV photolytic synthesis and γ-irradiation-induced decomposition of NF_4^+ salts. Furthermore, the fluorination of NF_3^+ to NF_4^+ appears to require F atoms.

(3) In the thermal decomposition of either NF_4BF_4 or NF_4AsF_6, BF_3 or AsF_5 acts as a strong rate suppressor, whereas both NF_3 and F_2 suppress the decomposition rates only mildly (see above results).

(4) Filtered UV radiation[4,8] or heating[9] to 120 °C supply sufficient activation energy for the formation of NF_4^+ salts. This is a strong indication that the first step in the synthesis must be the dissociation of F_2 into two fluorine atoms ($D°(F_2)$ = 36.8 kcal mol^{-1}).[16]

(5) The tendency to form NF_4^+ salts by thermal activation strongly decreases with decreasing Lewis acid strength, i.e., $SbF_5 > AsF_5 > PF_5 > BF_3$.[4,5,9] Since the corresponding NF_4^+ salts all possess sufficient thermal stability, a mechanism[3] involving the initial formation of NF_5, followed by its reaction with the corresponding Lewis acid, cannot explain the lack of thermal formation of salts such as NF_4PF_6 or NF_4BF_4. It can be explained, however, by the formation of intermediates of lower thermal stability such as NF_3^+ salts. For SbF_6^- or AsF_6^-, these NF_3^+ salts were shown to still possess the lifetime required for their efficient conversion to NF_4^+ salts, whereas $NF_3^+BF_4^-$ was found to be of considerably lower thermal stability.

(6) ESR flow-tube experiments[17] gave no indication of interaction between F atoms and AsF_5, as expected for the reaction step $AsF_5 + F \cdot \rightarrow AsF_6$.

(7) Infrared matrix isolation studies of the thermal decomposition products from either NF_4AsF_6[3] or $(NF_4)_2NiF_6$[18] gave no evidence for the formation of NF_5.

(8) Lewis acids such as BF_3, PF_5, AsF_5, or SbF_5 do not form stable adducts with NF_3, even at low temperatures.[19,20]

Since NF_3, F_2, and F have ionization potentials of 13.00,[20] 15.69,[21] and 17.44 eV,[22] respectively, any mechanism involving the initial formation of either NF_3^+, F_2^+, or F^+ can be ruled out, based on condition 4. This leaves us with Schemes I–IV as possibilities.

Scheme I

$$NF_3 + AsF_5 \rightarrow NF_3^+AsF_6^-$$
$$F_2 \rightarrow 2F\cdot$$
$$NF_3^+AsF_6^- + F\cdot \rightarrow NF_4^+AsF_6^- + \cdot$$
$$NF_3^+AsF_6^- + F\cdot \rightarrow NF_4^+AsF_6^- + \cdot$$

Scheme II

$$F_2 \rightleftarrows 2F\cdot$$
$$F\cdot + AsF_5 \rightleftarrows AsF_6\cdot$$
$$AsF_6\cdot + NF_3 \rightleftarrows NF_3^+AsF_6^-$$
$$NF_3^+AsF_6^- + F\cdot \rightleftarrows NF_4^+AsF_6^- + \cdot$$

Scheme III

$$F_2 \rightarrow 2F\cdot$$
$$F\cdot + NF_3 \rightarrow NF_4\cdot$$
$$NF_4\cdot + F\cdot \rightarrow NF_5$$
$$NF_5 + AsF_5 \rightarrow NF_4^+AsF_6^-$$

Scheme IV

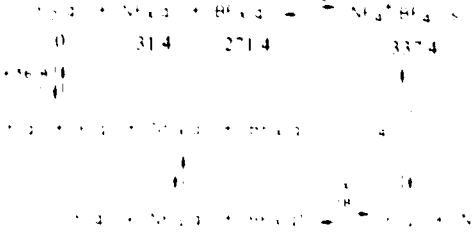
$$F_2 \rightarrow 2F\cdot$$
$$F\cdot + NF_3 \rightarrow NF_4\cdot$$
$$NF_4\cdot + AsF_5 \rightarrow NF_3^+AsF_6^- + \cdot$$
$$NF_3^+AsF_6^- + F\cdot \rightarrow NF_4^+AsF_6^- + \cdot$$

Scheme I can be ruled out because it does not comply with conditions 8 and 3. In Scheme I, NF_3 would be expected to suppress as strongly as AsF_5. Scheme II can be eliminated because of the fact that it violates condition 3 (i.e., NF_3 should be a stronger suppressor than AsF_5) and because of condition 6. Scheme III is unacceptable because it does not comply with conditions 2 and 5. Scheme IV is the only mechanism which agrees with all experimental data and therefore is our preferred mechanism. This mechanism differs from all the mechanisms previously proposed. It appears to be generally applicable to NF_4^+ salts, except for certain decomposition reactions in which NF_4^+ oxidatively fluorinates the anion.[18]

In view of the rather complex mechanism of Scheme IV and the observed fractional reaction order for the decomposition process, a mathematical analysis of the kinetic data was too complex and beyond the scope of the present study.

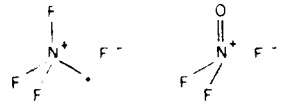
Born Haber Cycle for NF_4BF_4. It was of interest to examine the thermodynamic soundness of Scheme IV. NF_4BF_4 was chosen for this purpose because it is the only NF_4^+ salt for which the heat of formation has experimentally been determined.[23] The Born–Haber cycle is shown in Scheme V, where all heats of formation or reaction are given in kcal mol^{-1}. From the known heats of reaction of NF_3,[24] BF_3,[24] and NF_4BF_4,[23] the heat of reaction 5 is known to be −34.6 kcal mol^{-1}. Furthermore, the heat of dissociation of F_2, reaction 1, is known[16] to be 36.8 kcal mol^{-1}. A reasonably close estimate for step 3, the heat of formation of solid $NF_3^+BF_4^-$ from NF_4 and BF_3, can be made from the known heat of dissociation of $NF_2O^+BF_4^-$. Since NF_2O and NF_4 are expected to be quite similar (see below), it is reasonable to assume that step 3 has a heat of reaction similar to that of $NF_2O + BF_3 \rightarrow NF_2O^+BF_4^-$, i.e., −18 kcal mol^{-1}. Consequently, the sum of steps 2 and 4 should be about −53 kcal mol^{-1}. Whereas the heat of reaction of step 2 is difficult to estimate, the heat of

Scheme V



reaction of (4) is easier to estimate because it represents the dissociation energy of the fourth N-F bond in NF_4^+. In NF_3, the heat of dissociation of the third N-F bond is 58 kcal mol^{-1},[26,27] and it seems reasonable to assume that the dissociation energy of the fourth N-F bond in NF_4^+ is similar to or slightly less than this value. Consequently, step 2 should be approximately thermochemically neutral.

The proposition that steps 2 and 4 should so markedly differ in their heats of reaction, although both involve the formation of one additional N-F bond, is not unreasonable. In step 2 a hypervalent NF_4 radical is formed which would possess nine valence electrons on the central nitrogen atom. By analogy with the known NF_3O molecule,[28] this energetically unfavorable structure can be circumvented by assuming strong contributions from resonance structures such as



These resonance structures result in a strong polarization, i.e., weakening of all N-F bonds, when compared to those in NF_3. This is demonstrated by the bond lengths of 1.371 and 1.43 Å observed for NF_3[29] and NF_3O,[28] respectively. Thus the energy gained by the formation of a fourth N-F bond in the NF_4 radical is largely compensated by a significant weakening of the remaining N-F bonds. In contrast, the reaction of the NF_3^+ radical cation with a fluorine atom, i.e.

does not significantly change the nature of the existing N-F bonds and, therefore, is expected to result in a heat of reaction close to the energy of this bond.

An alternate, attractively simple, and preferable explanation for the above bond weakening effect in NF_4 can be offered if one assumes that, due to the large energy difference between the 2p and 3s nitrogen orbitals, the ninth nitrogen valence electron occupies an antibonding orbital. Experimental evidence for such a model has recently been reported[30] by Nishikida and Williams for the NF_3O^- radical anion which is isoelectronic with NF_4. On the basis of the observed ESR data, NF_3O^- possesses a spin density of 0.27 in the nitrogen 2s orbital suggesting that the unpaired electron indeed occupies an antibonding orbital.

A third possible, although less likely, explanation would be the assumption of a trigonal-bipyramidal structure for NF_4, in which two axial fluorines and nitrogen form a semiionic three-center, four-electron bond while the three equatorial positions are occupied by two fluorine ligands and the unpaired electron. Although all three models are basically a formalism describing the same net result, i.e., an increase of the bond length and ionicity of the NF bonds, model III should result in significantly different bond angles and therefore be experimentally distinguishable from models I and II.

It should be pointed out that the global activation energy (36.6 ± 0.8 kcal mol^{-1}) of the decomposition of NF_4BF_4 to $NF_3 + F_2 + BF_3$ and the heat of formation of NF_4BF_4 from $NF_3 + F_2 + BF_3$ (−34.6 kcal mol^{-1}) are the same within experimental error. It is difficult to say whether this is coincidental or if it implies that the corresponding forward reactions, i.e., steps 2–4 of the Born–Haber cycle, occur without activation energy. Examples of the latter case are known for the endothermic dissociation of solids such as carbonates.[31] If for NF_4^+ salts the global decomposition activation energies should indeed be identical with the heats of formation from NF_3, F_2, and the corresponding Lewis acid, a value of about −372 kcal mol^{-1} can be predicted for $\Delta H_f^\circ_{NF_4AsF_6}$ on the basis of $E_{NF_4AsF_6}$ = 45 kcal mol^{-1} and $\Delta H_f^\circ_{AsF_5}$ = 29.55 kcal mol^{-1}.

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Registry No. NF_4BF_4, 15640-93-4; NF_4AsF_6, 16871-75-3; NF_4SbF_6, 16871-76-4; NF_3, 7783-54-2; F_2, 7782-41-4; SbF_5, 7783-70-2.

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APPENDIX F

SIMPLIFIED SYNTHESIS OF $NF_4^+SBF_6^-$

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SHORT COMMUNICATION

Simplified Synthesis of $NF_4^+SbF_6^-$

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In NF_4^+ chemistry, the $NF_4^+SbF_6^-$ salt plays a key role. It is most amenable to large scale production and serves as a starting material for the metathetical syntheses of numerous other NF_4^+ salts [1 - 4]. The most convenient previously reported [5] method involved the reaction of SbF_5 with an excess of NF_3 and F_2 at elevated temperature and pressure according to:

$$NF_3 + F_2 + SbF_5 \xrightarrow[20\text{-}100\ atm]{250^\circ C} NF_4^+SbF_6^-$$

In view of its appreciable cost and its detremental physical and chemical properties, it was desirable to replace SbF_5 by a starting material which is cheaper, more readily available and easier to handle. Since it is well known [6] that, under conditions similar to those of the above NF_4SbF_6 synthesis, SbI_5 can be fluorinated by F_2 to SbF_5,

$$SbF_5 + F_2 \longrightarrow SbI_5$$

a direct synthesis of $NF_4^+SbF_6^-$ from SbI_5, F_2 and NF_3 was logical. The possible combination of the two steps was experimentally verified, as shown by the following equation:

$$NF_3 + 2F_2 + SbI_5 \xrightarrow[50\text{-}70\ atm]{250^\circ C} NF_4^+SbF_6^-$$

Although no efforts were made to maximize all the reaction parameters, the high yield and purity of the thus obtained $NF_4^+SbF_6^-$ demonstrates the feasibility of this simplified synthesis.

EXPERIMENTAL

A prepassivated (with ClF_3) 95 ml monel cylinder was loaded in the dry nitrogen atmosphere of a glove box with SbF_5 (31 mmol). The cylinder was connected to a metal vacuum system, evacuated, and charged at -196°C with NF_3 (65 mmol) and F_2 (98 mmol). The cylinder was heated for five days to 250°C. The excess of unreacted NF_3 and F_2 was pumped off at ambient temperature, leaving behind a white crystallinic residue (10 g, weight expected for 31 mmol of NF_4SbF_6=10.1 g). Based on its infrared and Raman stectra and its chemical analysis, this solid consisted of high purity $NF_4^+SbF_6^-$. It did not contain any detectable amounts of polyantimonate [7] salts.

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APPENDIX G

SYNTHESIS AND PROPERTIES OF $NF_4^+ClO_4^-$ AND $NF_4^+HF^-\cdot nHF$ AND SOME REACTION CHEMISTRY OF NF_4^+ SALTS

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SYNTHESIS AND PROPERTIES OF
$NF_4^+ClO_4^-$ AND $NF_4^+HF_2^-\cdot nHF$ AND SOME REACTION CHEMISTRY OF NF_4^+ SALTS

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Received . . . . .

Abstract

The possibility of synthesizing $NF_4^+XO_4^-$(X= Cl, Br, I) salts by metathesis between NF_4SbF_6 and $CsXO_4$ in anhydrous HF solution at -78° was studied. Of these NF_4XO_4 salts, NF_4ClO_4 was isolated and characterized by vibrational and ^{19}F NMR spectroscopy. It is an unstable white solid decomposing at 25° to give NF_3 and $FOClO_3$ in high yield. The NF_4BrO_4 salt is of marginal stability in HF solution and decomposes to NF_3, O_2 and $FBrO_2$. Attempts to isolate NF_4BrO_4 as a solid resulted in explosions. The NF_4IO_4 salt could not be prepared due to the facile fluorination of IO_4^- to $IF_4O_2^-$ by either HF or BrF_5. Attempts to prepare $NF_4^+XF_4O^-$ (X = Cl, Br) salts by metathesis between NF_4SbF_6 and $CsXF_4O$ in BrF_5 solution at 25° were unsuccessful; with BrF_4O^-, fluoride abstraction occurred resulting in the formation of NF_3, F_2, and BrF_3O, whereas $CsClF_4O$ underwent a displacement reaction with BrF_5 to give $CsBrF_6$ and ClF_3O. The metathetical synthesis of NF_4NO_3 could not be studied in HF due to the reaction of NO_3^- with HF to give NO_2^+, H_2O, and HF_2^-. The metathesis between NF_4SbF_6 and CsF in HF at -78° did not produce $NF_4^+F^-$, but an unstable white solid of the composition $NF_4^+HF_2^-\cdot nHF$. The composition, thermal stability, spectroscopic properties and decomposition products of this solid were studied.

The $NF_4^+HF_2^-$ salt is stable in HF solution at 25° and the synthetic usefulness of these solutions for the synthesis of other NF_4^+ salts is briefly discussed. Attempts to prepare NCl_4^+ and NCl_2O^+ salts by F-Cl exchange between BCl_3 and NF_4^+ and NF_2O^+ were unsuccessful.

Introduction

The first reports on the successful syntheses of NF_4^+ salts were published in 1966.[1,2] Since then, numerous NF_4^+ salts have been prepared and characterized which contain as counterions BF_4^-,[3-10] XF_5^- (X = Ge, Ti, Sn),[10-12] XF_6^- (X = P, As, Sb, Bi)[1,2,7,8,10,13,14-18] or XF_6^{--} (X = Ge, Sn, Ti, Ni).[10-12,19] All these anions are derived from strong perfluorinated Lewis acids. It was therefore interesting to investigate the possible synthesis of salts derived from either the simplest anion, F^-, or oxygen containing anions. Although in 1968 Tolberg and coworkers found evidence for the existence of unstable NF_4^+ salts probably containing the HF_2^- or the ClO_4^- anion,[4] these salts were not well characterized and no data were published. In this paper, we describe the synthesis and characterization of $NF_4^+HF_2^-\cdot nHF$ and $NF_4^+ClO_4^-$ and the attempted syntheses of $NF_4^+BrO_4^-$, $NF_4^+BrF_4O^-$, $NF_4^+ClF_4O^-$, and $NF_4^+NO_3^-$.[20] Since the existence of a stable $NOCl_2^+SbCl_6^-$ salt has recently been reported, it appeared interesting to study the possiblity of exchanging fluorine for chlorine in either NF_4^+ or NF_2O^+ salts using BCl_3.

Experimental

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[7] NF_2OSbF_6,[21] $CsClF_4O$,[22] and $CsBrF_4O$.[23] The BrF_5 (Matheson) was treated with 35 atm of F_2 at 200°C for 24 hours and then purified by fractional condensation through traps kept at -64° and -95°, with the material retained in the

latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_5 to remove the last traces of H_2O.[18] The CsF (American Potash) was fused in a platinum crucible and ground in the dry box. The $CsClO_4$ (ROC/RIC) was used as received. The $CsNO_3$ was prepared from aqueous Cs_2CO_3 and HNO_3 using a pH-electrode for endpoint detection. It was purified by recrystallization from H_2O and dried in an oven at 100°C for 24 hours. The BCl_3 (Matheson) was treated with Hg and purified by fractional condensation prior to use.

Apparatus. Volatile materials used in this work were handled either in a Monel-Teflon FEP, a stainless steel-Teflon FEP or a Teflon PFA vacuum line. The latter was constructed exclusively from injection molded PFA fittings and valves (Fluoroware, Inc.). The anhydrous HF was preferentially handled in the PFA or Monel line, whereas the halogen fluorides were handled mainly in a steel line. All lines were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Metathetical reactions were carried out either in HF or BrF_5 solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref. 12). For NMR or low temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4mm Teflon FEP or thin-walled Kel-F tube.

Infrared spectra were recorded in the range 4000-200cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Room temperature spectra of solids were obtained using dry powders pressed between AgCl disks. Low temperature spectra were obtained by placing the chilled powder between cold AgCl disks and striking the disks with a hammer. The resulting AgCl sandwich was held in a liquid N_2 cooled sample holder of a low-temperature infrared cell[24] with external CsI windows. Spectra of gases were obtained using a Teflon cell of 5cm pathlength equipped with AgCl windows.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter [25] for the elimination of plasma lines. Sealed quartz, Teflon FEP or Kel-F Tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described [26] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[25] Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer equipped with a variable temperature probe. Chemical shifts were determined relative to external $CFCl_3$.

Preparation and Properties of $NF_4^+ClO_4^-$. The compatibility of the ClO_4^- anion with HF was established by dissolving $CsClO_4$ in HF and recording the Raman spectra of the solution and of the solid residue recovered after removal of the solvent. Both spectra showed exclusively the bands characteristic for ClO_4^-. In a typical preparation of NF_4ClO_4, NF_4SbF_6 (10.03 mmol) and $CsClO_4$ (10.02 mmol) were placed into the 3/4" o.d. Teflon FEP bottom U-trap of the metathesis apparatus. Anhydrous HF (8.56 g) was added at -196°. The mixture was kept at -78° for 15 hours and then for 2 hours at -45° with agitation. The entire metathesis apparatus was cooled to -78° and inverted to separate the $CsSbF_6$ precipitate from the $NF_4^+ClO_4^-$ solution. Dry N_2 (2 atm) was used to pressurize the solution during this filtration step. The HF solvent was pumped off at -78° and -45° for 7 days. The resulting white solid residue was allowed to warm to ambient temperature and the gaseous decomposition products were separated in a dynamic vacuum by fractional condensation through a series of traps kept at -112°, -186° and -210°. The -210° trap contained 8.0 mmol of NF_3 and the -186° trap had 8.0 mmol of $FOClO_3$ which were identified by infrared, Raman and ^{19}F NMR spectroscopy. [27] The filter cake (3.60 g, weight calcd for 10 mmol of $CsSbF_6$ = 3.69 g) was shown by infrared and Raman spectroscopy to be $CsSbF_6$ and did not contain any detectable impurities. A small amount (80 mg) of a white stable solid residue was left behind after the thermal

decomposition of the NF_4ClO_4 which, based on its vibrational spectra, consisted of a mixture of NF_4SbF_6 and $CsSbF_6$. The 20% of NF_4ClO_4 unaccounted for by the above material balance corresponds to the amount of product in the mother liquor typically retained by the $CsSbF_6$ filter cake in similar metathetical reactions. It is decomposed and pumped off during the HF removal step in which the filter cake is allowed to warm to ambient temperature. Based on the above material balance, the NF_4ClO_4 prepared in this manner had a purity of 95 weight percent.

For the spectroscopic identification of NF_4ClO_4 and the determination of its thermal stability, reactions were carried out on a 1-2 mmol scale using 4 mm o.d. Teflon FEP NMR or thin walled Kel-F tubes as receivers. The ^{19}F NMR spectrum of an $NF_4^+ClO_4^-$ solution in anhydrous HF at -40° showed the signals characteristic of NF_4^+ (triplet of equal intensity at ϕ -214.8 with J_{NF} = 229.3 Hz and a linewidth of less than 3 Hz) [10], $FOClO_3$ (singlet at ϕ -219.4)[27], and NF_3 (broad triplet of equal intensity at ϕ -142 with J_{NF} = 150 Hz).[28,29] When the solution was kept at 20° and continuously monitored by NMR, the signal due to NF_4^+ was found to steadily decrease and those due to $FOClO_3$ and NF_3 to correspondingly increase in relative intensity. A solution containing 40 mol% of NF_4^+ and 60 mol% $FOClO_3$ was found to change within 16 hours at 20° to 17 mol% of NF_4^+ and 83 mol% of $FOClO_3$. The decomposition of NF_4ClO_4 in HF solution at ambient temperature was also followed by Raman spectroscopy which showed the bands due to $FOClO_3$ [27] to grow with time at the expense of those due to NF_4^+ and ClO_4^-. Due to its low boiling point and low solubility in HF, NF_3 could not be detected in the HF solution by Raman spectroscopy.

The thermal stability of solid $NF_4^+ClO_4^-$ was studied by pumping on a sample at a given temperature for one hour and measuring the amount of NF_3 and $FOClO_3$ evolved. Whereas at -13° NF_4ClO_4 essentially is still stable, slow decomposition was observed at 0° which became rather rapid at 25° giving the sample the appearance of a fluidized sand bath. Caution! Since the thermal decomposition of NF_4ClO_4 yields the very shocksensitive [30] $FOClO_3$ in high yield, appropriate safety precautions should be taken when working with this compound.

Reaction of NF_4SbF_6 with $CsBrO_4$. The compatibility of $CsBrO_4$ with HF was established in the same manner as described above for $CsClO_4$. The solubility of $CsBrO_4$ in HF at 25° was in excess of 1 g per g of HF. For the metathetical reaction, NF_4SbF_6 and $CsBrO_4$ (1.0 mmol each) in HF (2 ml) were stirred at 20° for 1.5 hours, then half of the solvent was pumped off and the mixture was cooled to -78° and filtered at this temperature into a Teflon FEP NMR tube. The NMR tube was sealed off, and the filter cake was pumped to dryness and shown by vibrational spectroscopy to consist of $CsSbF_6$. The Raman spectrum of the solution, which showed signs of gas evolution (O_2), exhibited the bands characteristic for NF_4^+, BrO_4^- [31] and $FBrO_2$ [32] with the intensity of the $FBrO_2$ bands growing with time at the expense of those of NF_4^+ and BrO_4^-. The ^{19}F NMR spectrum showed resonances characteristic of NF_4^+ (sharp triplet of equal intensity at ϕ -217 with J_{NF} = 227 Hz) and NF_3 (broad triplet of equal intensity at ϕ -143 with J_{NF} = 150 Hz) and a broad line at ϕ 186 attributed to HF (ϕ 196) undergoing rapid exchange with $FBrO_2$ (ϕ -205).[33] Caution! Explosions occurred when attempts were made to isolate solid NF_4BrO_4 from an HF solution which had never been warmed above -78°.

Reaction of $CsNO_3$ with HF. Cesium nitrate was dissolved in anhydrous HF. The Raman spectrum of the solution did not show the bands characteristic of NO_3^-, but only one band at 1411 cm^{-1} which is characteristic [34] for NO_2^+. The solid residue obtained by pumping the solution to dryness was shown by Raman spectroscopy to consist again of $CsNO_3$.

Reaction of NF_4SbF_6 with $CsBrF_4O$ in BrF_5. A mixture of NF_4SbF_6 (0.536 mmol) and $CsBrF_4O$ (0.449 mmol) was placed in the drybox into a 3/4" o.d. Teflon FEP ampule and BrF_5 (4 ml liquid) was added at -196° using the vacuum line. The contents of the ampule were warmed to 20° and stirred with a magnetic stirring bar for 2.5 hours. The ampule was cooled to -196° and the noncondensible material (0.42 mmol of F_2) was distilled off. The material volatile at -95° was distilled off and consisted of 0.48 mmol of NF_3. The material volatile at 20° was separated by fractional condensation through a series of traps kept at -64°, -78° and -196°. The -64° trap contained BrF_3O (0.43 mmol),

in addition to some BrF_5. The two colder traps contained the bulk of the BrF_5. The solid nonvolatile reaction product (205 mg, weight calcd for 0.449 mmol $CsSbF_6$ and 0.087 mmol NF_4SbF_6 = 194 mg) was shown by vibrational spectroscopy to consist mainly of $CsSbF_6$ containing some NF_4SbF_6.

Reaction of $CsClF_4O$ with BrF_5. In a sapphire reactor, $CsClF_4O$ (1.234 mmol) and BrF_5 (15 mmol) were combined at -196°. The mixture was kept at 20° for 12 hours. The volatile products were distilled off and consisted of BrF_5 and ClF_3O(1.2 mmol). The solid residue (405 mg, weight calcd for 1.234 mmol of $CsBrF_6$ = 403 mg) was shown by vibrational spectroscopy to consist of $CsBrF_6$.[35]

Preparation and Properties of $NF_4^+HF_2^-$·nHF. In a typical experiment, NF_4SbF_6 and CsF (10.0 mmol each) were placed into the metathesis apparatus and HF (10 ml) was added at -196°. The mixture was stirred at 20° for 2 hours, then cooled to -78° and filtered. Most of the HF solvent was removed by pumping at -78° for 36 hours, -64° for 12 hours, -57° for 6 hours and -45° for 6 hours. At -45° the residue was still liquid, but when cooled to -78° changed its appearance to that of a wet solid. The pumped off material consisted of HF. The sample was allowed to warm to ambient temperature and the evolved volatile material was pumped off through traps kept at -126°and -210°. The amounts and mole ratios of HF (-126° trap) and NF_3 (-210° trap) were periodically measured while cooling the sample back to -45°. Several hours of warming to ambient temperature and to 40° were required to achieve complete decomposition of the salt. A total of 8.32 mmol of NF_3 and 19.63 mmol of HF were collected with the HF:NF_3 mole ratio ranging from 10.1 at the start to 1.54 towards the end of the decomposition. A small amount (80 mg) of a stable white solid residue was left behind after completion of the decomposition which consisted mainly of NF_4SbF_6 and some $CsSbF_6$. The filter cake (3.5 g, weight calcd for 10.0 mmol of $CsSbF_6$ = 3.687 g) consisted of $CsSbF_6$. The 15% of NF_4^+ value unaccounted for by the above material balance is in line with the amount of material in the mother liquor generally retained by the $CsSbF_6$ filter cake in similar reactions (see NF_4ClO_4 preparation.)

Based on the above material balance, the purity of $NF_4HF_2 \cdot nHF$ obtained in this manner is about 97 mol% with the $CsSbF_6$ and NF_4SbF_6 impurities being caused by the slight solubility of $CsSbF_6$ in HF and a small excess of one reagent. During the above described ambient-temperature decomposition of $NF_4HF_2 \cdot nHF$, the originally liquid sample first turned milky and pasty, then after recooling it to -45° had the appearance of a white dry solid which melted very slowly when warmed again to 20°. On melting it started to bubble and foam.

For the determination of the spectroscopic properties, metathetical reactions were carried out as described above, but on a one mmol scale. The ^{19}F NMR spectrum of the compound in HF solution showed the signal (triplet of equal intensity at ϕ -216.2 with J_{NF} = 230 Hz and a line width of less than 3 Hz) characteristic[13,14] of NF_4^+ and a broad line at ϕ 195 due to rapidly exchanging HF and HF_2^-. The solution appeared to be stable at ambient temperature and no formation of the NF_3 decomposition product was detectable by NMR.

Raman spectra were recorded for the HF solutions at different concentration stages. In all cases, only the characteristic NF_4^+ bands at 1170, 859, 617 and 448 cm^{-1} were observed. For the most dilute solution also a very broad solvent band centered at about 3300 cm^{-1} was observed. After removal of most of the solvent at -57° the solvent band had disappeared. When this sample was frozen at -110°, numerous intense bands in the 1400 - 1700 and the 650 - 850 cm^{-1} region appeared. However, on further removal of HF, the spectrum of the solid at -110° showed again only bands due to NF_4^+ .

Reactions of NF_4SbF_6 and NF_2OSbF_6 with BCl_3. A sample of NF_4SbF_6 (1.85 mmol) was treated in a Teflon FEP ampule with a tenfold excess of BCl_3 for three hours at 20°. The volatile products were separated by fractional condensation and shown to consist of NF_3 and mixed BF_xCl_{3-x} type compounds. A small amount of solid residue (60 mg) was identified by vibrational spectroscopy as $NO^+SbCl_6^-$.

A sample of NF_2OSbF_6 was similarly treated with BCl_3. The volatile products consisted again of mixed BF_xCl_{3-x} type compounds, but $NO^+SbF_6^-$ was formed in almost quantitative yield as a nonvolatile residue.

Results and Discussion

The general usefulness of the metathetical reaction

$$NF_4^+SbF_6^- + Cs^+X^- \xrightarrow[-78^\circ]{HF} Cs^+SbF_6^-\downarrow + NF_4^+X^-$$

for the syntheses of otherwise inaccessible $NF_4^+X^-$ salts has previously been demonstrated[7,11,12,18,19] for a number of perfluorinated anions. In this study this approach was extended to oxygen containing anions, such as the perhalates and tetrafluorohalates.

Synthesis and Properties of NF_4ClO_4. The ClO_4^- anion was found to be stable in HF solution. Therefore, NF_4ClO_4 was prepared according to

$$NF_4SbF_6 + CsClO_4 \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4ClO_4$$

The reaction must be carried out at low temperature since, even in HF solution, NF_4ClO_4 undergoes decomposition at room temperature. The NF_4ClO_4 salt can be isolated as a white solid, stable up to about -13°. At 0° slow decomposition and at 25° rapid decomposition of the solid was observed according to

$$NF_4ClO_4 \longrightarrow NF_3 + FOClO_3$$

In HF solution the rate of decomposition is slower, but follows the same path. The essentially quantitative formation of $FOClO_3$ is noteworthy and represents a new and convenient synthesis of $FOClO_3$.

Based on the observed material balance, the yield of NF_4ClO_4 is high and the only significant loss of material is due to the amount of mother liquor retained by the $CsSbF_6$ filter cake. The purity of the NF_4ClO_4 product is also high and the impurities present are $CsSbF_6$, in an amount corresponding to its solubility in HF at -78°, and any slight excess of starting material used in the reaction.

The ionic composition of NF_4ClO_4, both in HF solution and the solid state, was established by vibrational and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of $NF_4^+ClO_4^-$ in HF solution showed the signal characteristic[13,14] for tetrahedral NF_4^+. The Raman spectra of this solution confirmed the presence of tetrahedral NF_4^+ (1170 w, br, 855 vs, p, 612 m, 448 mw)[10] and ClO_4^- (940s, p, 620w, 460w)[34]. The infrared and Raman spectra of solid $NF_4^+ClO_4^-$ are given in Figure 1, together with the observed frequencies and their assignments in point group T_d. As expected for a solid, splittings of some bands into their degenerate components and crystal splittings are observed. In addition $\nu_1(A_1)$ and $\nu_2(E)$ which ideally are infrared inactive were observed in the infrared spectrum as extremely weak bands. The pronounced Christiansen effect[36] observed for the infrared spectrum is due to the experimental difficulties in obtaining good pressing of AgCl windows at low temperature. The pressing was achieved by striking the sample sandwiched between the AgCl plates with a hammer. The sample did not detonate under these conditions indicating that NF_4ClO_4 is considerably less sensitive than its decomposition product $FOClO_3$.[30]

Reaction of NF_4SbF_6 with $CsBrO_4$. The BrO_4^- anion was found to be stable in HF solution, thus allowing the metathetical reaction

$$NF_4SbF_6 + CsBrO_4 \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4BrO_4$$

to be carried out.

The presence of tetrahedral NF_4^+ [10,13,14] and BrO_4^- [31] in the resulting HF solution was demonstrated by ^{19}F NMR and Raman spectroscopy. By analogy with NF_4ClO_4, slow decomposition of the NF_4BrO_4 solution occurred at room temperature. However, instead of the yet unknown $FOBrO_3$, only its expected[37] decomposition products, $FBrO_2$ and O_2, were obtained in addition to NF_3.

$$NF_4BrO_4 \longrightarrow NF_3 + [FOBrO_3]$$

$$[FOBrO_3] \longrightarrow FBrO_2 + O_2$$

Attempts to isolate solid NF_4BrO_4 from an HF solution, which had never been warmed above -78°, were unsuccessful due to a sharp detonation of the sample with flashing. Whether this was caused by NF_4BrO_4 itself or possibly by the presence of some $FOBrO_3$ could not be established.

The metathetical synthesis of NF_4IO_4 was not possible due to the fact that IO_4^- interacts with either HF[27,38] or BrF_5[27] according to

$$IO_4^- + 4HF \longrightarrow IF_4O_2^- \text{ (cis and trans isomer)} + 2H_2O$$

$$IF_4O_2^- + 2HF \longrightarrow HF_2^- + HOIF_4O$$

$$IO_4^- + 2BrF_5 \longrightarrow IF_4O_2^- \text{ (trans isomer mainly)} + 2BrF_3O$$

The metathesis between $CsIF_4O_2$ and NF_4SbF_6 in HF, followed by the thermal decomposition of the metathesis product, produces the novel compounds, cis- and trans- OIF_4OF, and will be reported in a separate paper.

Reaction of NF_4SbF_6 with $CsBrF_4O$. Although $CsBrF_4O$ reacts with HF[39] according to

$$CsBrF_4O + HF \longrightarrow CsHF_2 + BrF_3O$$

BrF_5 does not interact with $CsBrF_4O$ [23] and therefore is a suitable solvent for studying the reaction of NF_4SbF_6 with $CsBrF_4O$. The following reaction was observed

$$CsBrF_4O + NF_4SbF_6 \xrightarrow[25^o]{BrF_5} CsSbF_6 + BrF_3O + F_2 + NF_3$$

The formation of these products indicates that the salt $NF_4^+BrF_4O^-$ is not stable under these conditions and that, contrary to the $NF_4^+ClO_4^-$ and $NF_4^+IF_4O_2^-$ reactions, fluoride abstraction from BrF_4O^- is preferred over the fluorination of BrF_4O^- to either BrF_4OF or BrF_5O. A similar fluoride abstraction has previously been observed [4] for BrF_6^-

$$NF_4SbF_6 + CsBrF_6 \xrightarrow[25^o]{BrF_5} CsSbF_6 + NF_3 + F_2 + BrF_5$$

but not for BrF_4^- which was fluorinated [4] to BrF_5

$$NF_4SbF_6 + KBrF_4 \xrightarrow[25^o]{BrF_5} KSbF_6 + NF_3 + BrF_5$$

The corresponding metathesis between $CsClF_4O$ and NF_4SbF_6 was not studied because it was found that $CsClF_4O$ reacts with BrF_5 according to

$$CsClF_4O + BrF_5 \longrightarrow CsBrF_6 + ClF_3O$$

The formed $CsBrF_6$ would be capable of undergoing with NF_4SbF_6 the above given fluoride abstraction reaction.

Reaction of $CsNO_3$ with HF. The compatibility of $CsNO_3$ with HF was studied in order to explore the feasibility of synthesizing NF_4NO_3. Although $CsNO_3$ is quite soluble in HF and can be recovered as such from HF solutions, Raman spectra of these solutions showed the absence of NO_3^- and the presence of NO_2^+ as the only nitrogen oxygen containing species.

These results imply an equilibrium, such as

$$NO_3^- + 4HF \rightleftharpoons NO_2^+ + H_2O + 2\ HF_2^-$$

which has previously been postulated[40] for these solutions. In view of the absence of NO_3^- in HF solution, no metathetical reactions between $CsNO_3$ and NF_4SbF_6 were attempted.

Preparation and Properties of $NF_4HF_2 \cdot nHF$. The $NF_4^+F^-$ salt, which has an active fluorine content in excess of 90 weight percent, would be of extreme interest. However, previous attempts to prepare this salt from NF_3 and F_2 at -196° by either bremsstrahlung[3] or uv-photolysis[10] were unsuccessful indicating that the salt is unstable with regard to its decomposition to NF_3 and F_2. The instability of $NF_4^+F^-$ can be explained by the small size of the F^- anion resulting in an insufficient lattice energy to stabilize the salt.[3] However, the anion size and thereby the lattice energy can be sufficiently increased by the addition of F^- to a Lewis acid, such as BF_3 or MF_5 (M = P, As, Sb, or Bi). Since most of the metathetical reactions for the production of NF_4^+ salts are carried out in anhydrous HF, which is an acid, it was of interest to define the nature and stability of a possible $NF_4^+HF_2^-$ salt. A previous unpublished study[4] of the LiF - NF_4SbF_6 system in HF at ambient temperature had provided evidence that after removal of the precipitated $LiSbF_6$ a stable solution was obtained containing the NF_4^+ cation. All attempts to isolate a salt at temperatures of -44° and above from this solution resulted in decomposition to NF_3, F_2 and HF. Removal of the solvent at -78° resulted in a wet solid which was not characterized.

Since our previous studies[18] had shown that a low-temperature metathesis using a cesium salt is superior to a lithium salt based process, the following system was studied

$$NF_4SbF_6 + CsHF_2 \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4HF_2$$

Based on the observed material balance, the soluble product consisted of about 97 mole% NF_4HF_2 with the remainder being $CsSbF_6$ and excess of either starting material. In agreement with the previous observation[4], NF_4HF_2 is stable in HF solution at ambient temperature and shows in the ^{19}F NMR spectrum the characteristic[13,14] NF_4^+ signal. The presence of the NF_4^+ cation and the virtual absence of anions other than those due to solvated F^- was also demonstrated by Raman spectroscopy of solutions at different concentrations. As shown by trace A of Figure 2, these solutions exhibited only the four bands characteristic[10] of tetrahedral NF_4^+. The difficulty in observing bands due to solvated HF_2^- is not surprising in view of HF being a weak scatterer and the expected broadness of the lines of HF_2^- undergoing rapid exchange with the solvent HF.

Most of the solvent can be removed by pumping at -45°. The resulting residue is a clear liquid at -45°, but solidifies at -78° to give the appearance of a wet solid. The composition of this residue was determined by studying its exhaustive dissociation at 25° according to

$$NF_4HF_2 \cdot nHF \longrightarrow NF_3 + F_2 + (n+1)HF$$

It was found that the mole ratio of NF_3:HF was about 10.1 at the beginning and 1.54 towards the end of this decomposition. These results demonstrate that complete removal of solvated HF from NF_4HF_2 is extremely difficult and is accompanied by decomposition of most of the NF_4^+ salt itself. The presence of a solvated $HF_2^- \cdot nHF$ anion was also demonstrated by Raman spectroscopy (see trace B of Figure 2) which shows the presence of broad complex bands in the vicinity of the symmetric (600 cm^{-1}) and the antisymmetric (1455 cm^{-1}) stretching mode[34] of HF_2^-. Upon removal of most of the solvated HF, these bands lost intensity, resulting in a spectrum consisting exclusively of the NF_4^+ bands (see trace C of Figure 2).

It is also noteworthy that with decreasing HF content, the melting point of $NF_4^+HF_2^-\cdot nHF$ increases and approaches room temperature for n approaching zero. The decomposition of $NF_4HF_2\cdot nHF$ becomes rather slow for decreasing n, particularly in the presence of other stable fluorides. It appears that such fluorides can assume the function of stabilizing the HF_2^- anion. A typical example for such a fluoride is AlF_3 or AlF_4^-.[27] A careful analysis of such systems is therefore necessary to avoid the interpretation of such $(NF_4HF_2)_nMF_x$ in terms of $(NF_4)_nMF_{x+n}$ salts.

The possibility of preparing stable HF solutions of NF_4HF_2 renders them a very useful intermediate. By addition of a stronger or less volatile Lewis acid, the HF_2^- anion can be displaced and NF_4HF_2 can be converted into other NF_4^+ salts. This was first demonstrated[24] by reacting NF_4HF_2 solutions with BF_3 to form NF_4BF_4, and has recently been extended[41] to the formation of other salts, which due to the low solubility of their cesium salts are not amenable to direct metathetical reactions.

Halogen Exchange in NF_4^+ and NF_2O^+. In view of the existence of a stable $NCl_2O^+SbCl_6^-$ salt[20], it was of interest to study the possibility of halogen exchange in either NF_4^+ or NF_2O^+ with BCl_3. For both salts, the observation of mixed BF_xCl_{3-x} products indicated that halogen exchange took place. For NF_4^+ the main product was gaseous NF_3 suggesting that the likely NF_3Cl^+ intermediate might be unstable towards decomposition under the given conditions. For $NF_2O^+SbF_6^-$, the main product was $NO^+SbF_6^-$ which could arise again from breaking of the rather weak N-Cl bonds in an NCl_2O^+ intermediate.

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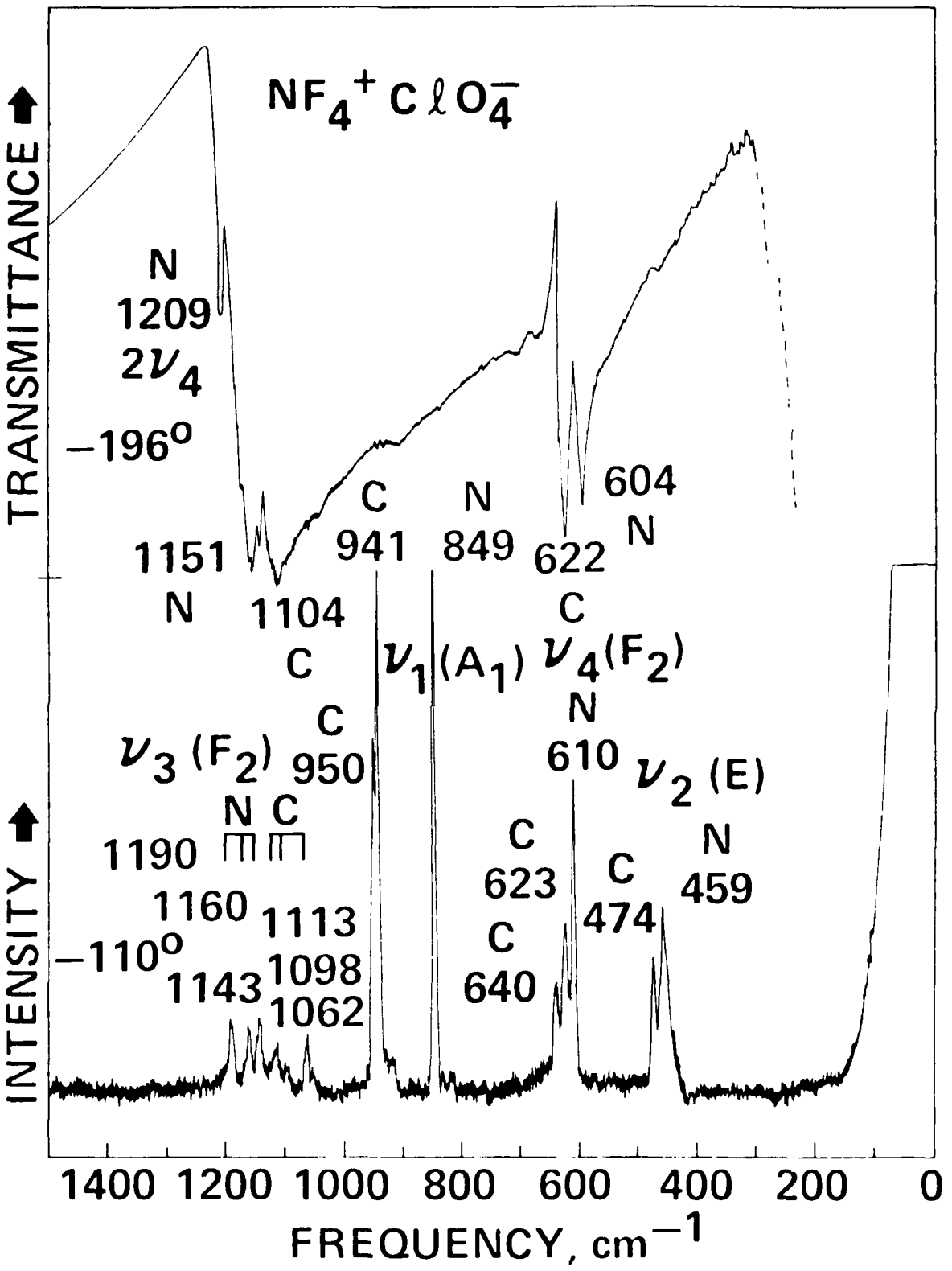
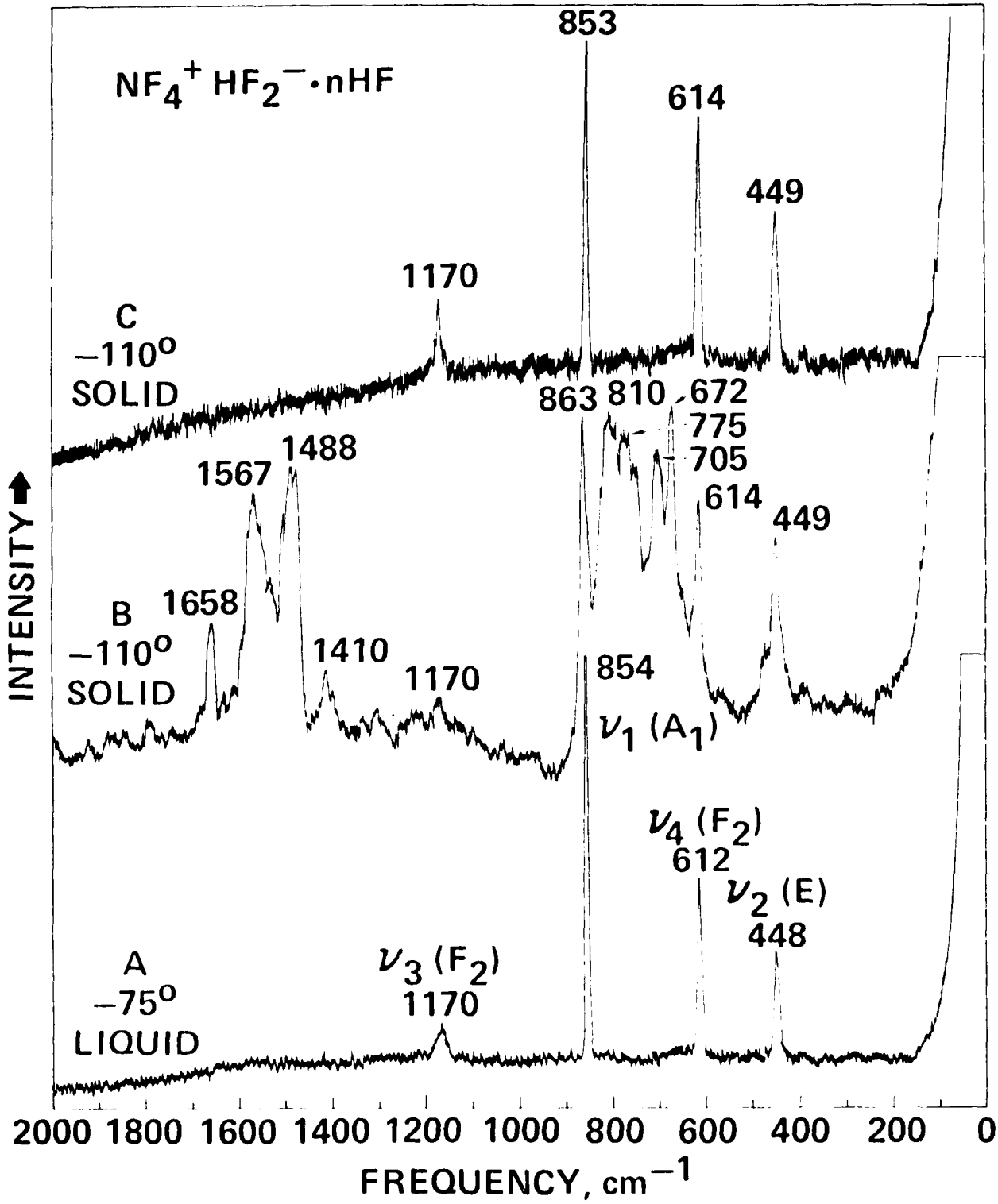
Diagram Captions

Figure 1. Low-temperature vibrational spectra of solid $NF_4^+ClO_4^-$. The infrared spectrum was recorded as a dry powder between AgCl disks. The broken line indicates absorption due to the AgCl window material. The Raman spectrum was recorded with a spectral slit width of 6 cm^{-1}. The given assignments are for ideal tetrahedral NF_4^+ cations (N) and ClO_4^- anions (C) ignoring site symmetry and solid state effects.

Figure 2. Raman spectra of liquid and solid $NF_4^+HF_2^-\cdot nHF$ in a Kel-F capillary. Trace A, spectrum of a concentrated HF solution at -75°. The given assignments are for tetrahedral NF_4^+. Trace B, sample of trace A cooled to -110°. In addition to the NF_4^+ bands, the spectrum shows bands attributed to $HF_2^-\cdot nHF$. Trace C, spectrum of the solid at -110° containing only a small excess of HF. The sample of trace B was used after pumping off most of the HF and decomposing most of the sample at about -20°. All spectra were recorded with a spectral slit width of 8 cm^{-1}.


$NF_4^+ Cl O_4^-$
TRANSMITTANCE
INTENSITY
N
1209
$2\nu_4$
−196°
1151
N
1104
C
C
941
N
849
622
C
604
N
$\nu_1(A_1)$
$\nu_4(F_2)$
N
610
$\nu_3(F_2)$
C
950
$\nu_2(E)$
N C
1190
1160
1113
−110°
1143
1098
1062
C
623
C
640
C
474
N
459
1400 1200 1000 800 600 400 200 0
FREQUENCY, cm^{-1}


$NF_4^+ HF_2^- \cdot nHF$
853
614
449
1170
C
−110°
SOLID
863
810
672
775
705
614
449
1567
1488
INTENSITY
B
−110°
SOLID
1658
1410
1170
854
ν_1 (A_1)
ν_4 (F_2)
612
ν_2 (E)
448
A
−75°
LIQUID
ν_3 (F_2)
1170
2000 1800 1600 1400 1200 1000 800 600 400 200 0
FREQUENCY, cm^{-1}

APPENDIX H

SYNTHESIS AND PROPERTIES OF $NF_4^+SO_3F^-$

Contribution from Rocketdyne, A Division of
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Abstract

The novel salt $NF_4^+SO_3F^-$ was prepared by metathesis between NF_4SbF_6 and $CsSO_3F$ in anhydrous HF solution at -78°. In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid which is stable at 0°, but slowly decomposes at +10° to produce $FOSO_2F$ and NF_3 in high yield. The ionic nature of the compound, both in the solid state and in HF solution, was established by Raman and ^{19}F NMR spectroscopy. Cesium sulfate was found to react with anhydrous HF producing $CsSO_3F$ as the major product. Similarly, $CsPO_2F_2$, the Raman spectrum of which is reported, was found to react with HF to give $CsPF_6$ in quantitative yield.

Introduction

Among oxidizers, the NF_4^+ cation is unique. In spite of being one of the most powerful oxidizers known, it possesses high kinetic stability,[1] thereby permitting its combination with a surprisingly large number of anions to form stable or metastable salts. Anions capable of NF_4^+ salt formation include BF_4^-,[2-9] XF_5^-(X=Ge,Ti,Sn),[9-11] XF_6^-(X=P,As,Sb,Bi),[6,7,9,12-19] XF_6^{2-}(X=Ge,Sn,Ti, Ni,Mn),[6,10,11,19] ClO_4^-,[9-11,20,21] HF_2^-,[22] and several perfluoro polyanions.[22] Recent studies have shown that NF_4^+ salts of oxygen containing anions are of particular interest because hypofluorites, such as OIF_4OF[23] or $FOClO_3$[22], can be formed during their thermal decomposition.

In this paper we would like to report results on the possible synthesis of salts derived from sulfur or phosphorus oxyfluorides. We are aware of only

one unpublished study[3] in this area, in which the evolution of some $FOSO_2F$ from either an NF_4SbF_6-$HOSO_2F$ solution at -78° or a supposedly dry mixture of NF_4SbF_6 and $LiSO_3F$ at room temperature was interpreted[3] as evidence that NF_4SO_3F, if it exists, is unstable even at -78°. In view of the relative stability of NF_4ClO_4[22] and the similarity between ClO_4^- and isoelectronic SO_3F^- and $PO_2F_2^-$, the isolation of NF_4SO_3F and $NF_4PO_2F_2$ seemed possible.

Experimental

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.[22] Literature methods were used for the synthesis of NF_4SbF_6,[6] $ClOSO_2F$[24] and $HOPOF_2$[25]. The $CsPO_2F_2$ was prepared by the addition of Cs_2CO_3 to a 10% excess of $HOPOF_2$ frozen at -196°. The mixture was allowed to react at room temperature with agitation, and the volatile products and excess $HOPOF_2$ were pumped off at 40° for 12. hours. Based on the observed material balance and vibrational spectra, the solid residue consisted of $CsPO_2F_2$ of high purity. The Cs_2SO_4 was obtained from aqueous Cs_2CO_3 and H_2SO_4 using a pH-electrode for endpoint (pH of 3.86) detection. The solution was taken to dryness and dried in an oven at 100° for 24 hours. The $CsSO_3F$ was prepared by allowing CsCl (10.3 mmol) and $ClOSO_2F$ (15.5 mmol) to react in a 10 ml stainless steel cylinder at ambient temperature for several days. All volatile material was removed from the cylinder, and the solid product was pumped on overnight. The weight of the solid (2.43 g vs. 2.40 g theoretical) together with its infrared and Raman spectra confirmed the completeness of the reaction and the identity of the product.

Preparation and Properties of $NF_4^+SO_3F^-$. The compatibility of the SO_3F^- anion with HF was established by dissolving $CsSO_3F$ in dry HF and recording the Raman spectra of the starting material, the HF solution, and of the solid residue recovered after removal of the solvent. All spectra showed the bands characteristic[26] for SO_3F^-. The ^{19}F NMR spectrum of the HF solution was also recorded and consisted of a singlet at ϕ 33.8 (downfield from external $CFCl_3$) for SO_3F^- and a relatively narrow HF solvent peak at ϕ-191.

In a typical preparation of NF_4SO_3F, NF_4SbF_6 (3.145 mmol) and $CsSO_3F$ (3.146 mmol) were combined in a previously described[22] Teflon metathesis apparatus. Dry HF[22] (3 ml liquid) was added and the resulting mixture was stirred at ambient temperature for 3 hours with a magnetic stirring bar, followed by cooling to -78° and filtration at this temperature. The HF solvent was pumped off from the filtrate at -30° for 3 hours leaving behind a white solid residue. The thermal stability of this residue was established by incremental warm up of the solid in a dynamic vacuum and by trapping, measuring (PVT) and identifying (infrared spectroscopy) the volatile decomposition products. Up to 0°, only HF and small amounts of NF_3 were collected indicating the possible presence of small amounts of unstable $NF_4HF_2 \cdot nHF$[22] in the product. At temperatures of 9° or higher, significant decomposition of the solid was observed, producing equimolar amounts of NF_3 and $FOSO_2F$. Allowing for about 20% of the product solution being retained, as generally seems to be the case with similar metathetical reactions,[22] by the filter cake and being lost during solvent pump-off, the yield of NF_3 and $FOSO_2F$ was essentially quantitative. The filtercake (1.0 g, weight calcd for 3.15 mmol of $CsSbF_6$ = 1.10 g) was shown by vibrational spectroscopy to be $CsSbF_6$[28] and did not show any detectable impurities.

Caution! $FOSO_2F$ has been reported [29,30] to have explosive properties. The compound should therefore be handled with appropriate safety precautions.

For the spectroscopic identification of NF_4SO_3F, reactions were carried out on a 1 mmol scale in a previously described[22] manner. The ^{19}F NMR spectrum of a solution of $NF_4^+SO_3F^-$ in HF at -30° showed the signals characteristic for NF_4^+ (triplet of equal intensity at ϕ -215 with J_{NF} = 226 Hz and a linewidth of less than 3 Hz),[9] SO_3F^- (singlet at ϕ -33.5), and HF (broad singlet at ϕ 193). No evidence for the presence of $FOSO_2F$[27] was observed. The Raman spectra of the HF solution at 25° and of solid NF_4SO_3F at -100° were also recorded and are shown in Figure 1. The spectra showed the presence of only small amounts of $CsSbF_6$[28] indicating a purity of NF_4SO_3F in excess of 90 weight percent, in agreement with the observed material balance. Raman and ^{19}F NMR spectra of HF solutions of NF_4SO_3F, which were kept at 25° for several days, showed no evidence of $FOSO_2F$ formation.

Reaction of Cs_2SO_4 with HF. The Cs_2SO_4 salt was found to be highly soluble in HF. Raman spectra of these solutions and of the solid residue obtained after the solvent removal, showed the complete absence of the SO_4^{--} anion[28] and the presence of the SO_3F^- anion[26]. The presence of the SO_3F^- anion in the HF solution was confirmed by ^{19}F NMR spectroscopy which showed a strong singlet at ϕ -55.8, characteristic for SO_3F^-.

Reaction of $CsPO_2F_2$ with HF. A sample of $CsPO_2F_2$ (2.1 mmol) was treated with anhydrous HF (3 ml liquid) for 12 hours at 25°. The white solid residue, left behind after removal of the solvent, was identified by its infrared and Raman spectrum as $CsPF_6$[28] (2.1 mmol) and did not contain detectable amounts of $PO_2F_2^-$.[31 - 33]

Results and Discussion

The novel salt $NF_4^+SO_3F^-$ was prepared from NF_4SbF_6 and $CsSO_3F$ by low-temperature metathesis in anhydrous HF solution according to:

$$NF_4SbF_6 + CsSO_3F \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4SO_3F$$

The NF_4SO_3F salt can be isolated as a white solid which is stable at 0°, but slowly decomposes at +10° to produce NF_3 and $FOSO_2F$ in high yield according to

$$NF_4SO_3F \longrightarrow NF_3 + FOSO_2F$$

Its HF solution appears to be stable at ambient temperature. The thermal stability of NF_4SO_3F is very similar to that[22] of NF_4ClO_4. This is not surprising since SO_3F^- and ClO_4^- are isoelectronic and chemically very similar. This chemical similarity is also demonstrated by their decomposition modes, which in both cases produce the corresponding hypofluorites in high yield.

The decomposition of $NF_4^+SO_3F^-$ represents a new, high yield, convenient synthesis of $FOSO_2F$. The previously reported methods for the preparation of $FOSO_2F$ involved either the fluorination of SO_3[34,35] or $S_2O_6F_2$[36]. NF_4SO_3F is the third known example of an NF_4^+ salt of an oxy-anion producing on thermal decomposition the corresponding hypofluorite. The other two known examples are NF_4ClO_4[22] and

$NF_4IF_4O_2$.[23] This indicates that the thermal decomposition of unstable NF_4^+ salts of oxy-anions may be a general method for the synthesis of hypofluorites.

The ionic nature of NF_4SO_3F, both in the solid state and in HF solution, was verified by Raman and ^{19}F NMR spectroscopy. The Raman spectra are shown in Figure 1 and demonstrate the presence of the bands characteristic for NF_4^+ [9,22] and SO_3F^-.[26] The observed frequencies and their assignments are summarized in Table I. The SO_3F^- bands in NF_4SO_3F are very similar to those observed for $CsSO_3F$ (see Figure 1). The minor frequency shift observed for the SF stretching mode is not surprising in view of a previous infrared study of the alkali metal salts which showed that the frequency of this fundamental strongly depends on the nature of the cation and varied from 812 cm^{-1} in $LiSO_3F$ to 715 cm^{-1} in $CsSO_3F$.[26] The observed splitting of some of the modes of both the NF_4^+ cation and the SO_3F^- anion into their degenerate components is easily explained by solid state effects and has also been observed for $NF_4^+ClO_4^-$.[22]

The ^{19}F NMR spectrum of $NF_4^+SO_3F^-$ in HF solution showed a triplet of equal intensity at Ø-215 with J_{NF} = 226 Hz and a linewidth of less than 3Hz, characteristic for NF_4^+, a singlet at Ø-33.5, characteristic[9] for SO_3F^-, and the characteristic HF signal at Ø 193. The assignment of the Ø-33 signal to SO_3F^- was verified by recording the spectrum of $CsSO_3F$ in HF under the same conditions.

In view of the above mentioned usefulness of NF_4^+ salts of oxy-anions for the preparation of novel hypofluorites, it appeared interesting to attempt the syntheses of $(NF_4)_2SO_4$ and $NF_4PO_2F_2$. The thermal decomposition of these two hypothetical salts would offer an opportunity to prepare the yet unknown hypofluorites, $SO_2(OF)_2$ and $POF_2(OF)$. However, both the SO_4^{--} and $PO_2F_2^-$ anion were found to interact with anhydrous HF according to:

$$SO_4^{--} + 3HF \longrightarrow SO_3F^- + H_2O + HF_2^-$$

and

$$PO_2F_2^- + 4HF \longrightarrow PF_6^- + 2H_2O$$

Attempts to prepare $POF_2(OF)$ by fluorination of $HOPOF_2$ with atomic fluorine, generated by the controlled decomposition of $NF_4HF_2 \cdot nHF$,[22] were also unsuccessful. The main products were NF_4PF_6[9] and an unidentified nonvolatile phosphorus oxyfluoride.

Although vibrational spectra have been reported[31-33] for the $PO_2F_2^-$ anion, the previous assignment of several fundamentals is open to question. Figure 2 and Table 2 summarize the vibrational spectra of $CsPO_2F_2$, obtained in our study. The given assignment was made by analogy with that of isoelectronic SO_2F_2 which is well established.[37-39] Whereas, the splitting of $\nu_8(B_2)$ can easily be explained by Fermi resonance with $\nu_4+\nu_9(B_2)$, the reason for the observed splitting of ν_4 is less obvious. The possibility of one of the components assigned to ν_4 actually being due to the $\nu_5(A_2)$ torsional mode cannot be ruled out, but is unlikely due to the facts that this mode should be infrared inactive under C_{2v} selection rules and usually is of such low intensity in the Raman spectra that it is very difficult to observe.

In summary, the present study shows that within the isoelectronic series, ClO_4^-, SO_3F^-, $PO_2F_2^-$, SO_4^{--}, the first two anions are capable of forming NF_4^+ salts of moderate stability which can decompose to NF_3 and the corresponding hypofluorites. The syntheses of $NF_4PO_2F_2$ and $(NF_4)_2SO_4$ by metathesis in HF was prevented by the reaction of $PO_2F_2^-$ and SO_4^{--} with the solvent to yield PF_6^- and SO_3F^-, respectively.

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Table I. Raman Spectra of NF_4SO_3F and $CsSO_3F$

Obsd freq, cm^{-1}, and rel intens[a]

NF_4SO_3F		$CsSO_3F$	Assignment (point group)	
HF solution	solid	solid	$NF_4^+(T_d)$	$SO_3F^-(C_{3v})$
	1277 (0.7)	1278 (0.7)		$\nu_4(E)$
	1267 (0.4)			
1165 (0.4)	1166 (1.3)		$\nu_3(F_2)$	
	1152 (1.8)			
1087 (6.7)p	1083 (10)	1076 (10)		$\nu_1(A_1)$
853 (10)p	850 (9.5)		$\nu_1(A_1)$	
	749 (1.1)	719 (1.2)		$\nu_2(A_1)$
	738 (0.8)			
612 (3)	612 (6)		$\nu_4(F_2)$	
575 (1.2)	584 (1.7)	582 (2)		$\nu_5(E)$
	563 (2.5)	560 (2.2)		$\nu_3(A_1)$
446 (2.8)	450 (4)		$\nu_2(E)$	
400 (1)	415 (2.5)	406 (3.8)		$\nu_6(E)$
	404 (2.3)	396 (3.5)		

(a) uncorrected Raman intensities

Table II. Vibrational Spectra of Solid $CsPO_2F_2$ and Their Assignment Compared to Those of SO_2F_2

Obsd freq, cm^{-1} and rel intens				Assignment (point group C_{2v})		Approximate description of mode
$CsPO_2F_2$[a]		SO_2F_2[b]				
Raman	IR	Raman	IR			
1145 (10)	1142 vs	1270 vs	1270 vs	A_1	ν_1	sym. PO_2 stretch
813 (3.7)	825 vs	848 vs	848 vs		ν_2	sym. PF_2 stretch
512 (6)	520 sh	552 m	553 s		ν_3	δ scissoring PO_2
370 sh	370 mw	394 m	394 vw		ν_4	δ scissoring PF_2
355 (5.7)	351 mw					
--	--	[384±15][c]		A_2	ν_5	τ
1318(0+)	1325 vs	1504 w	1503 vs	B_1	ν_6	asym. PO_2 stretch
591 (2)	494 s	539 m	540 s		ν_7	δ rock PF_2
851 (0.7)	850 sh	888 w	886 vs	B_2	ν_8	asym. PF_2 stretch[d]
830 (1.2)	825 vs					
501 (2)	508 s	544 m	544 s		ν_9	δ rock PO_2

(a) data from this study; uncorrected Raman intensities; since ν_7 and ν_9 have very similar frequencies and intensities, their assignments are tentative.

(b) data from ref. 36-38

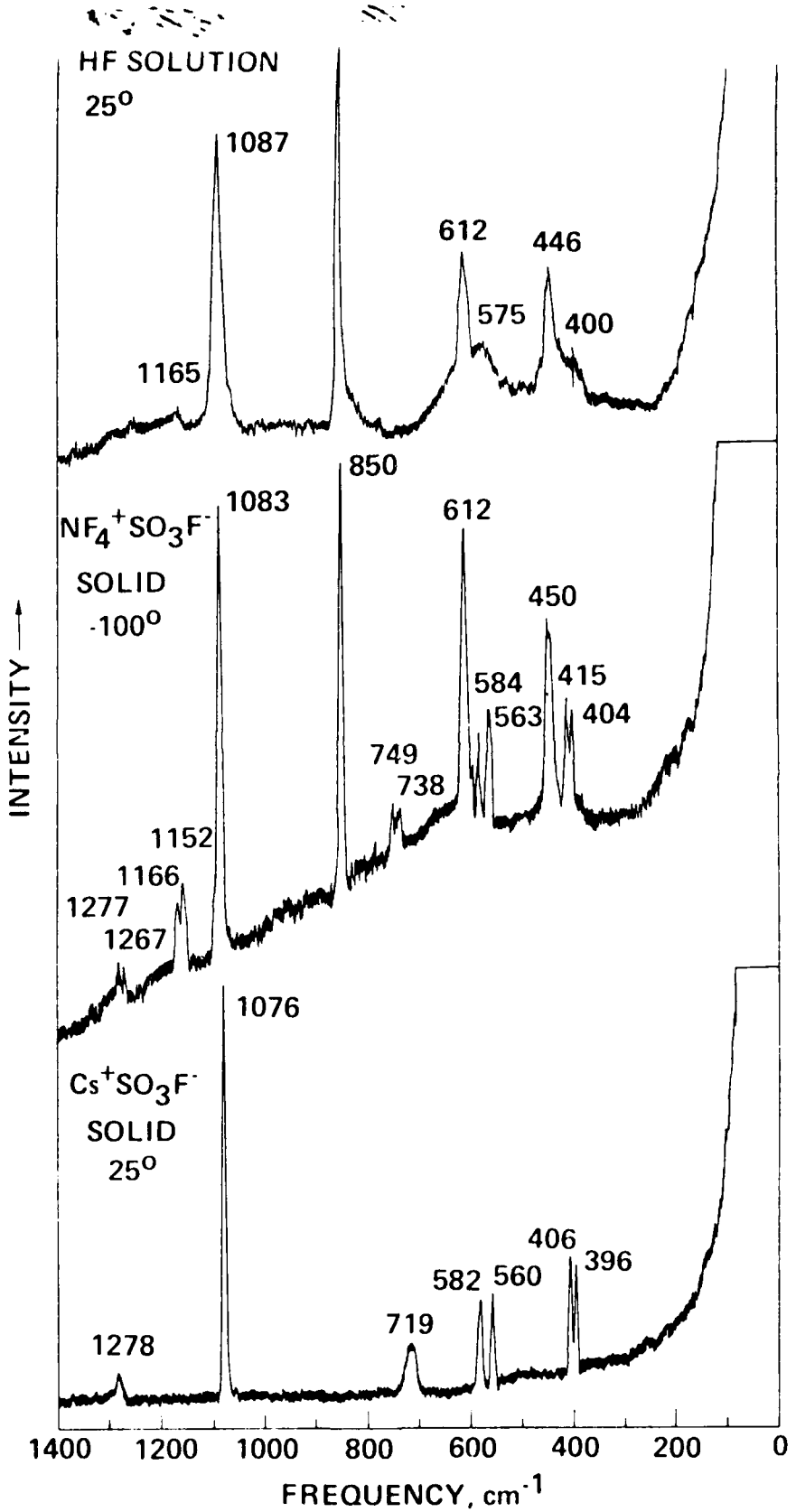
(c) from microwave data, ref. 37

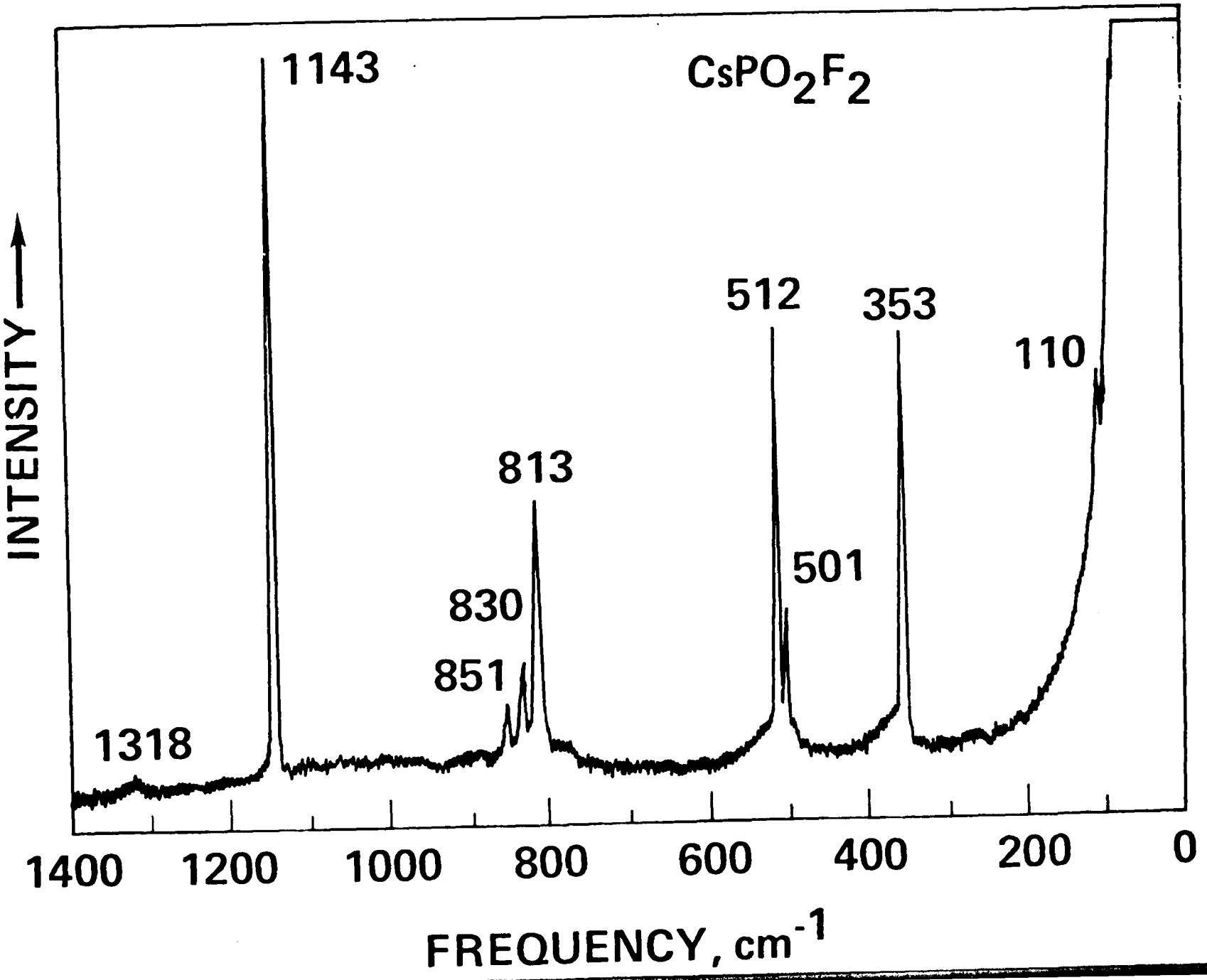
(d) in Fermi resonance with $\nu_4+\nu_9(B_2)$ = 851 cm^{-1}

Diagram Captions

Figure 1. Raman spectra of $NF_4^+SO_3F^-$. Upper trace, HF solution at 25°, middle trace, neat solid at -100°. Weak bands due to the sample tubes and small amounts of $CsSbF_6$ were subtracted from the spectra. Bottom trace, solid $CsSO_3F$ at 25°. The spectra were recorded with spectral slitwidths of 8, 6 and 4 cm^{-1}, respectively.

Figure 2. Raman spectrum of solid $CsPO_2F_2$ recorded at 25° with a spectral slit width of 5 cm^{-1}.


HF SOLUTION
25°
1087
612
446
575
400
1165
850
1083
612
$NF_4^+SO_3F^-$
SOLID
-100°
450
584
415
563
404
749
738
1152
1166
1277
1267
1076
$Cs^+SO_3F^-$
SOLID
25°
406
396
582
560
719
1278
INTENSITY
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm^{-1}



RI/RD80-157

H-13/H-14

APPENDIX I

SYNTHESIS AND PROPERTIES OF $NF_4^+UF_5O^-$

William W. Wilson, Richard D. Wilson and Karl O. Christe*

Received . . . . .

Abstract

A new method for the synthesis of NF_4^+ salts is reported. It permits the synthesis of otherwise inaccessible salts derived from nonvolatile Lewis acids which do not possess HF - soluble cesium salts. The method was successfully applied to the synthesis of the novel salt $NF_4^+UF_5O^-$. This compound is a yellow solid, stable at room temperature. It was characterized by analysis and vibrational spectroscopy.

Introduction

Most NF_4^+ salts, derived from volatile strong Lewis acids, can be prepared directly from NF_3, F_2 and the Lewis acid in the presence of a suitable activation energy source [1,2]:

$$NF_3 + F_2 + XF_n \xrightarrow{\Delta E} NF_4^+ XF_{n+1}^-$$

If the Lewis acid is polymeric and nonvolatile, its NF_4^+ salt can usually be prepared by an indirect metathetical process [3,4], provided a compatible solvent is available in which the starting materials are soluble and one of the products is insoluble. This metathetical approach has been demonstrated for several NF_4^+ salts [3 - 7]. A typical example is the synthesis of $(NF_4)_2NiF_6$ in anhydrous HF solution [7] using the cesium salts. The latter salts are preferred because they exhibit the most favorable solubility products for a metathesis in HF[4]:

$$Cs_2NiF_6 + 2NF_4SbF_6 \xrightarrow[-78^o]{HF} 2CsSbF_6\downarrow + (NF_4)_2NiF_6$$

However, in cases where the corresponding cesium salt starting material or both products are insoluble in the solvent and the Lewis acid is nonvolatile, neither one of the above approaches can be used. In this paper a method which circumvents these problems is described and is applied to the synthesis of the novel salt $NF_4^+UF_5O^-$.

Experimental

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described [8]. Literature methods were used for the syntheses of UF_4O[9], KUF_5O[10], and NF_4SbF_6[3]. The CsF (American Potash) was fused in a platinum crucible and ground in the dry box. The HF (Matheson) was dried by treatment with F_2, followed by storage over BiF_5 to remove last traces of water [4].

Preparation and Properties of $NF_4^+UF_5O^-$. In a typical experiment, a solution of NF_4HF_2 (12.5 mmol) in anhydrous HF (12.5g) was prepared from NF_4SbF_6 and CsF at -78°, as previously described [8], and added to UOF_4 (6.18 mmol). The resulting mixture was kept at -78° for 40 hours, then warmed to -31° for 6 hours with stirring, followed by removal of all volatile products in vacuo by slowly raising the temperature from -31° to 20°C. A yellow solid residue (2.70 g, weight calcd for 6.18 mmol of NF_4UF_5O=2.71 g) was obtained. This compound was stable at ambient temperature and of low solubility in HF. It was identified by elemental analysis and vibrational spectroscopy as $NF_4^+UF_5O^-$. For the elemental analysis, a weighed amount of sample was hydrolyzed in H_2O and the NF_3 evolution was measured [12]. The hydrolysate was analyzed for Cs and Sb by atomic absorption spectroscopy, and for U gravimetrically as U_3O_8. Based on this analysis, the composition (weight %) of the yellow solid was: NF_4UF_5O, 96.8; NF_4SbF_6, 1.7; $CsSbF_6$, 1.4.

The thermal decomposition of $NF_4^+UF_5O^-$ was studied in a sapphire reactor, equipped with a pressure transducer. The onset and rate of decomposition was determined by total pressure measurements [13] in a closed system over the temperature range 40-60°C. For the determination of the decomposition products,

a sample of NF_4UF_5O (2 mmol) was rapidly heated to 150°C in a dynamic vacuum, and the volatile products were collected in traps, cooled to -126° and -210°C, and were identified by their infrared spectra. The -126°C trap contained 1.1 mmol of UF_6, and the contents of the -210°C trap consisted of 1.5 mmol of NF_3 and a small amount of OF_2. The infrared spectrum of the pale yellow solid residue (350 mg) showed strong bands characteristic for UF_4O [9], UO_2F_2[14], NF_4^+ [2 - 8], and two broad bands at 520 and 410 cm^{-1}, probably due to UF_n vibrations. In addition, the spectrum indicated the presence of a small amount of UF_5O^- [10,11].

Results and Discussion

Synthesis. The metathetical synthesis of NF_4UF_5O according to

$$NF_4SbF_6 + MUF_5O \xrightarrow{HF} MSbF_6\downarrow + NF_4UF_5O$$

was not possible because both the MUF_5O (M = alkali metal) and NF_4UF_5O salts possess very low solubilities in anhydrous HF. Furthermore, in agreement with a previous report [10], we could not prepare a well defined $CsUF_5O$ salt by the reaction of CsF with UF_4O in anhydrous HF solution. The product always contained a large amount of unreacted UF_4O. Attempts to obtain reasonably pure NF_4UF_5O by a metathetical reaction using stoichiometric amounts of UF_4O, CsF, and NF_4SbF_6 in HF as starting materials, were also unsuccessful due to the unfavorable solubilities. However, preparation of an HF solution of NF_4HF_2 [8] according to

$$NF_4SbF_6 + CsHF_2 \xrightarrow[-78^\circ]{HF} NF_4HF_2 + CsSbF_6\downarrow$$

followed by removal of the insoluble $CsSbF_6$ by filtration at -78° and addition of this solution to UF_4O, resulted in NF_4UF_5O of about 97% purity.

$$NF_4HF_2 + UF_4O \xrightarrow{HF} NF_4UF_5O + HF$$

A twofold excess of NF_4HF_2 was used to ensure complete conversion of UF_4O to UF_5O^-. After solvent removal, the excess of unreacted NF_4HF_2 was decomposed [8] at 40°C to NF_3, F_2 and HF which were pumped off.

Properties. NF_4UF_5O is a yellow, crystallinic solid, stable up to about 50°C. Its composition was established by elemental analysis. The ionic nature of the salt was demonstrated by vibrational spectroscopy which showed the presence of the NF_4^+ cation and UF_5O^- anion. For comparison, a sample of KUF_5O was prepared from KF and UF_4O in HF, as previously reported [10]and its spectra were also recorded. The infrared spectra of NF_4UF_5O and KUF_5O are shown in Figure 1, and the observed infrared and Raman frequencies are summarized in Table 1. Whereas the infrared spectrum of KUF_5O is in good agreement with those[10,11] previously reported, the recording of a Raman spectrum with the available exciting line (4880Å) was very difficult due to fluorescence, strong color and poor scattering. For NF_4UF_5O, a similar, but not quite as severe, problem existed. Based on some of the Raman bands, observed for UF_5O^- in NF_4UF_5O, and by comparison with the well defined infrared bands, it appears that some of the Raman bands previously reported [10]for KUF_5O are open to question.

The assignments of the bands due to NF_4^+ are well established [2-8]and require no further discussion. For the UF_5O^- anion, only the stretching vibrations can be assigned with some confidence. The band in the 810-835 cm^{-1} region occurs at too high a frequency for a U-F stretching mode and, therefore, is assigned to the UO stretch. The intensity and band width of the 580-600 cm^{-1} band in both the infrared and Raman spectra are comparable to those of the UO stretch and is therefore, assigned to the unique UF stretching mode. The broad intense infrared band at about 490 cm^{-1} should represent the antisymmetric UF_4 stretch, and the strong Raman band at about 490 cm^{-1} is assigned to the symmetric in-phase UF_4 stretching mode. The weak infrared band at about 430 cm^{-1} could be due to either the symmetric out-of-phase UF_4 stretching mode $\nu_5(B_1)$,(assuming that for the solid the site symmetry of UF_5O^- is lower than C_{4v}),or the OUF_4 deformation mode $\nu_9(E)$. However, for the latter assignment, the frequency appears somewhat high and is shifted in the wrong direction when going from KUF_5O to NF_4UF_5O. Due to the stronger anion-cation interaction in KUF_5O, the stretching modes are expected to be shifted to lower and the deformation modes to higher frequencies.

The thermal decomposition of NF_4UF_5O was studied in more detail since the decomposition of NF_4^+ salts containing oxyanions has been shown [8, 15, 16]

to be a useful synthetic route to hypofluorites. The NF_4UF_5O salt is stable up to about 50°C, but started to decompose in a sapphire reactor at 60°C at an approximately linear rate, resulting in a pressure build-up of about 4.6 mm Hg per hour for a 2 mmol sample in a 38.7 cc volume. The nature of the decomposition products was established by rapid pyrolysis at 150°C in a dynamic vacuum. The main decomposition products, condensible at -210°C, were NF_3, UF_6, and a small amount of OF_2. The pale yellow solid residue contained UF_4O and UO_2F_2 as the major products. The formation of UF_4O, UF_6 and UO_2F_2 as main decomposition products can be readily explained by assuming

$$NF_4UF_5O \rightarrow NF_3 + F_2 + UF_4O$$

as the primary decomposition step, followed by the well established [9, 17] decomposition of UF_4O

$$2UF_4O \rightarrow UF_6 + UO_2F_2$$

The fact that the recovered amount of UF_6 exceeded that expected from this reaction sequence, can readily be explained by partial fluorination of UF_4O or UF_5O^- by the formed elemental fluorine.

Conclusion. The results of this study show that NF_4^+ salts which are derived from nonvolatile polymeric Lewis acids and are insoluble in HF, are accessible by treating the corresponding Lewis acid with an excess of NF_4HF_2 in HF solution. Although this approach has so far been demonstrated only for UF_4O, it might be of general use.

Acknowledgement. The authors are grateful to Drs. C. J. Schack and L. R. Grant for helpful discussions, to Mr. R. Rushworth for the elemental analyses, and to the Office of Naval Research, Power Branch, and the Army Research Office for financial support.

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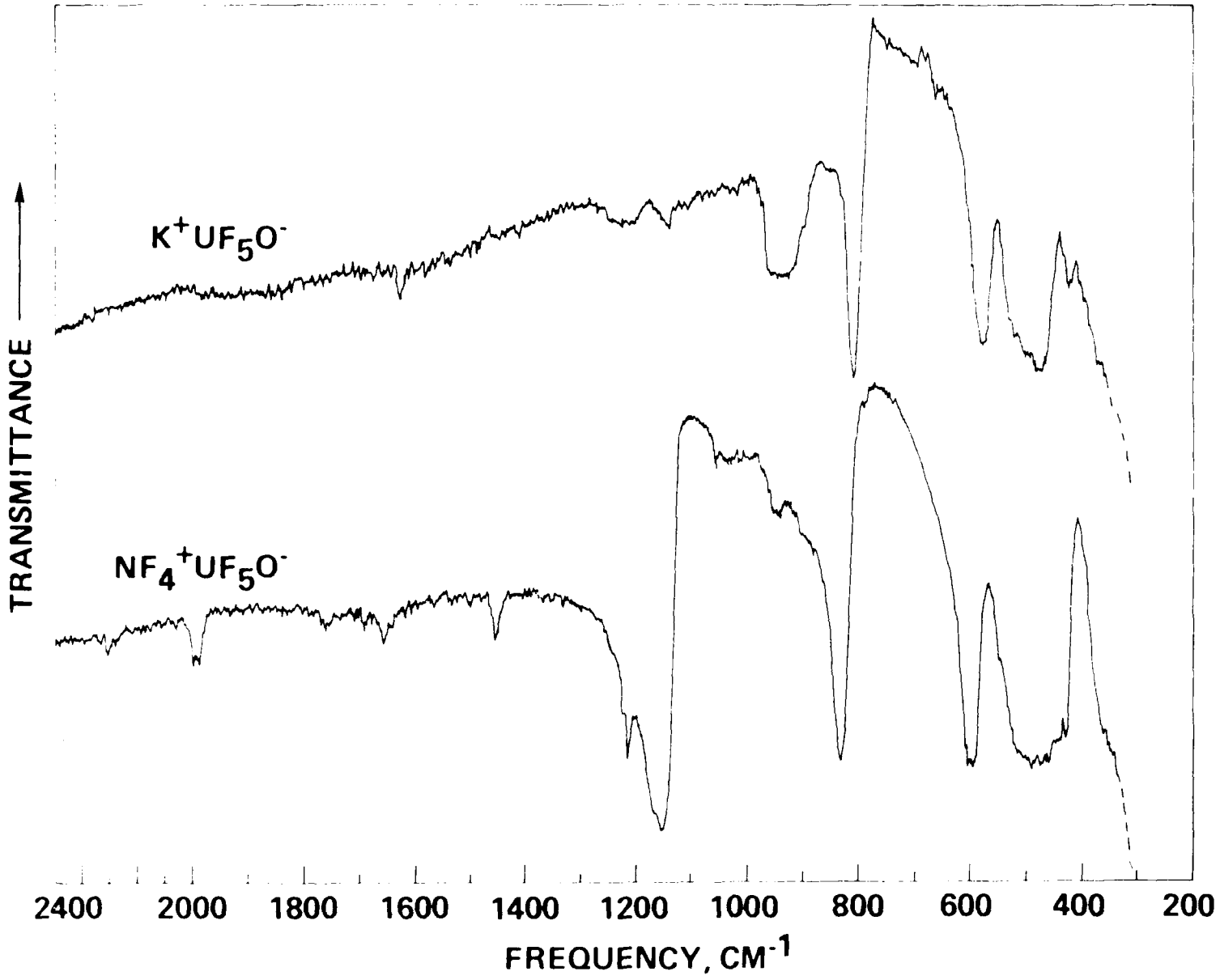
Diagram Caption

Figure 1. Infrared spectra of KUF_5O and NF_4UF_5O recorded as dry powders pressed between AgCl disks. The broken lines represent absorption due to the AgCl window material.


$K^+UF_5O^-$
$NF_4^+UF_5O^-$
TRANSMITTANCE
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY, CM^{-1}

APPENDIX J

SYNTHESIS AND CHARACTERIZATION OF $(NF_4)_2 MnF_6$

Karl O. Christe*, William W. Wilson and Richard D. Wilson

Received . . . .

Abstract

The synthesis of novel NF_4^+ salts containing doubly or triply charged third row transition metal fluoride anions, was studied. The new compound $(NF_4)_2MnF_6$ was prepared and characterized. The combination of good thermal stability and high active fluorine content makes $(NF_4)_2MnF_6$ an outstanding solid oxidizer.

Introduction

Due to the high energy content and high kinetic stability of the NF_4^+ cation,[1] NF_4^+ salts are important high-energy oxidizers, particularly for applications, such as solid propellant NF_3-F_2 gas generators.[2-4] In order to maximize the NF_3-F_2 yields available from such salts, it is desirable to combine as many NF_4^+ cations as possible with a given anion. Furthermore, the anion should be as light as possible, contribute to the fluorine generation, and decompose to a nonvolatile fluoride, i.e. be "self-clinkering".[4] Of the presently known NF_4^+ salts,[5] $(NF_4)_2NiF_6$[6] has the highest active fluorine content and is self-clinkering. However, its marginal thermal stability limits its potential applications. Consequently, compounds of comparable fluorine content, but possessing better thermal stability, are highly desirable. This paper describes the results of a systematic study on the synthesis of NF_4^+ salts, derived from third row transition metal fluorides, and the successful synthesis of the novel $(NF_4)_2MnF_6$ salt.

Experimental

Materials and Apparatus. The equipment, handling techniques and spectrometers used in this study have previously been described.[1,5] A literature method[7]

was used for the synthesis of NF_4SbF_6. For the synthesis of Cs_2MnF_6, a previously reported method[8] was slightly modified. Anhydrous $MnCl_2$ and dry CsF, in a 1:2 mol ratio, were fluorinated in a Monel cylinder at 400°C for 36 hours using a $MnCl_2$:F_2 mol ratio of 1:10. Based on the observed material balance, elemental analysis, X-ray diffraction powder pattern, and vibrational spectra, the resulting yellow solid consisted of high purity Cs_2MnF_6.

The Cs_2CuF_6 salt was prepared by high pressure fluorination of a mixture of CsF and $CuCl_2$ in a 2:1 mol ratio. The conditions (400°C, 18 hours, 130 atm) were similar to those[9] previously reported. However, during unsuccessful attempts to prepare Cs_3CuF_6 in a similar manner, it was noticed that very mild fluorination conditions (flow reactor, 200°C) sufficed to prepare Cs_2CuF_6. This brick-red compound was always formed as the major product, instead of the pale green Cs_3CuF_6. At the lower fluorination temperatures, the fluorination product also contained $CsClF_4$. The infrared spectrum of Cs_2CuF_6 showed major bands at 670, 570, 480 and 430 cm^{-1}. The compatibility of Cs_2CuF_6 with different solvents was studied. In BrF_5, Cs_2CuF_6 is stable but highly insoluble, whereas in anhydrous HF, it is soluble but undergoes a reaction even at -78°C resulting in the formation of a brown solid. When the Cs_2CuF_6-HF solutions were warmed to room temperature, fluorine evolution was observed, in agreement with a previous report.[10]

Preparation of $(NF_4)_2MnF_6$. Inside the N_2 atmosphere of a dry box a mixture of NF_4SbF_6 (37.29 mmol) and Cs_2MnF_6 (18.53 mmol) was placed into the bottom of a prepassivated (with ClF_3) Teflon FEP double U-tube metathesis apparatus.[8] Dry HF[11] (20 ml liquid) was added at -78°C on the vacuum line, and the mixture was warmed to 25°C for 30 min with stirring. The mixture was cooled to -78°C and pressure filtered at this temperature. The HF solvent was pumped off at 30°C for 12 hours. The white filter-cake (14 g, weight clcd for 37.1 mmol of $CsSbF_6$=13.7 g) was shown by Raman spectroscopy to consist mainly of $CsSbF_6$. The yellow filtrate residue (6.1 g, weight clcd for 18.5 mmol of $(NF_4)_2MnF_6$=6.46 g) was shown by elemental analysis to have the following composition (weight %): $(NF_4)_2MnF_6$, 91.27; NF_4SbF_6 4.27; $CsSbF_6$ 4.46. For the elemental analysis, a sample of $(NF_4)_2MnF_6$ was hydrolyzed in H_2O, the NF_3 and O_2 evolution was measured by PVT and gas chromatography, and Cs, Sb, and Mn in the hydrolysate were determined by atomic absorption spectroscopy.

Caution! The reaction of $(NF_4)_2MnF_6$ with H_2O is extremely violent, and proper safety precautions must be used.

The CoF_3-NF_4HF_2 System. A suspension of CoF_3 (231 mg = 2 mmol) in a freshly prepared concentrated NF_4HF_2-HF solution[5] (15 mmol of NF_4HF_2) was stirred at -45°C for 4 hours. The tan colored CoF_3 did not appear to react, and no evidence for the formation of pale blue CoF_6^{3-} was observed. The HF solvent was pumped off while allowing the mixture to warm slowly towards ambient temperature. At this temperature, the $NF_4HF_2 \cdot nHF$ underwent decomposition and was also pumped off. To assure complete decomposition of NF_4HF_2, the mixture was warmed to 45°C for 4 hours in a dynamic vacuum. The tan solid residue (250 mg) was shown by vibrational spectroscopy to be unreacted CoF_3.

Results and Discussion

In view of the marginal thermal stability of $(NF_4)_2NiF_6$ it was interesting to investigate the possibility of synthesizing other NF_4^+ salts containing multiply charged anions derived from higher oxidation state transition metal fluorides. It was hoped to obtain a salt which would be comparable to $(NF_4)_2NiF_6$ in its active fluorine content, but possess better thermal stability. The following anions were considered most promising: CuF_6^{3-}, NiF_6^{3-}, CoF_6^{3-}, MnF_6^{3-}, CuF_6^{2-}, CoF_6^{2-}, and MnF_6^{2-}.

Attempted Syntheses of $(NF_4)_3MF_6$ Salts. In a previous study,[10] it was shown that all these triply charged anions undergo solvolysis in HF. Furthermore, it was found that CuF_6^{3-} decomposed with F_2 evolution, and NiF_6^{3-} disproportionated with NiF_6^{2-} formation, but that for CoF_6^{3-} the solvolysis to $CoF_4 + 2HF_2^-$ could be suppressed by the addition of a 10 to 20 fold excess of fluoride ion to the solution. In view of these results, a simple metathetical reaction of an MF_6^{3-} salt in HF solution according to

$$3NF_4SbF_6 + Cs_3MF_6 \xrightarrow{HF} 3CsSbF_6\downarrow + (NF_4)_3MF_6$$

is preempted by the unavoidable solvolysis of MF_6^{3-}. However, the synthesis of a CoF_6^{3-} salt might be possible in the presence of a large excess of fluoride

ion, provided the excess of fluoride can be readily removed from the product. Such a method was recently discovered[12] and successfully applied to the synthesis of NF_4UF_5O according to

$$NF_4HF_2 + UF_4O \xrightarrow{HF} NF_4UF_5O + HF$$

NF_4HF_2 is thermally unstable[5] and decomposes at 30°C to NF_3, F_2 and HF, which are all gases. Therefore, the HF solvent can be pumped off first at low temperature, followed by decomposition and removal of the excess NF_4HF_2. Application of this method to the synthesis of $(NF_4)_3CoF_6$ according to

$$3NF_4HF_2 + CoF_3 \xrightarrow[-45^{o}]{HF} (NF_4)_3CoF_6 + 3HF$$

was unsuccessful, and no evidence for the formation of a cobalt containing NF_4^+ salt was obtained. Only unreacted CoF_3 was recovered.

Syntheses of $(NF_4)_2MF_6$ Salts. Since the MF_6^{2-} anions contain one negative charge less than the MF_6^{3-} ones, they are less basic and, therefore, are less likely to undergo solvolysis in the strongly acidic solvent HF. The compatibility of TiF_6^{2-} and NiF_6^{2-} with HF has previously been demonstrated[6,10,13] and led to the successful syntheses of $(NF_4)_2TiF_6$[13] and $(NF_4)_2NiF_6$[6]. During this study the compatibility of Cs_2CuF_6 with HF was studied. It was found that Cs_2CuF_6 reacts, even at low temperature, with HF to form a dark brown solid. At room temperature, decomposition with fluorine evolution occurs. The compatibility of Cs_2CoF_6 with HF was not examined since Court had previously shown[10] that this salt is unstable in HF solution.

In agreement with a previous report [10], MnF_6^{2-} was found to be stable in HF solution. Consequently, the following metathetical reaction

$$2NF_4SbF_6 + Cs_2MnF_6 \longrightarrow 2CsSbF_6\downarrow + (NF_4)_2MnF_6$$

was carried out which resulted in the isolation of the novel $(NF_4)_2MnF_6$ salt. This salt was obtained in high yield with a purity in excess of 90%. Since the by-products NF_4SbF_6 and $CsSbF_6$ are well characterized, no attempts were undertaken to purify the compound by well established[7] recrystallization techniques.

Properties of $(NF_4)_2MnF_6$. The $(NF_4)_2MnF_6$ salt is a yellow, crystallinic solid which is highly soluble in anhydrous HF. At 24°C, its solubility exceeds 1.30 g per g HF. It is stable at room temperature and, in the absence of fuels, it is not shock sensitive. With water a violent reaction occurs, similar to that previously reported[6] for $(NF_4)_2NiF_6$. By analogy with the other known NF_4^+ salts, the hydrolysis was found to result in quantitative NF_3 evolution and therefore, is a useful analytical method. The hydrolysis also produced oxygen in a $NF_3:O_2$ mole ratio of 8:5 in excellent agreement with the following equation:

$$4(NF_4)_2MnF_6 + 10H_2O \longrightarrow 8NF_3 + 5O_2 + 20HF + 4MnF_3$$

Thermal Decomposition. At 65°C, $(NF_4)_2MnF_6$ appears to be stable, but at about 100° it starts to slowly decompose. Its decomposition rate in a sapphire reactor was monitored by total pressure measurements over the temperature range 100 to 130°C. Except for a slightly faster rate during the first 20 minutes, the decomposition pressures increased approximately linearly with time at 100°C. At 130°C the rates slightly accelerated with increasing time, however, this rate increase was quite small. At 100°C 0.17% of the sample decomposed in 17 hours, whereas, at 130°C 0.66% of the sample decomposed in the same time. The gaseous decomposition products consisted of NF_3 and F_2 in a mol ratio of about 1 to 1.2. For identification of the solid residue, a sample of $(NF_4)_2MnF_6$ was completely decomposed in a dynamic vacuum at 240°C. Based on its weight, X-ray powder diffraction pattern[14] and mauve color, this residue was identified as MnF_3. Consequently, $(NF_4)_2MnF_6$ decomposes according to

$$2(NF_4)_2MnF_6 \longrightarrow 4NF_3 + 5F_2 + 2MnF_3$$

A comparison with the decomposition data previously published[6] for $(NF_4)_2NiF_6$ shows that the thermal stability of $(NF_4)_2MnF_6$ is significantly higher than that of $(NF_4)_2NiF_6$ which in 6 hours at 100°C exhibited 9% decomposition.

Crystallographic Data. The X-ray powder diffraction pattern of $(NF_4)_2MnF_6$ is listed in Table 1. The pattern was indexed in the tetragonal system and

shows that the compound is isotypic with the other known $(NF_4)_2MF_6$ (M=Ti, Ni, Ge, Sn)[6,8,13,15] salts (see Table 2). As expected, the size of the unit cell decreases from $(NF_4)_2TiF_6$ to $(NF_4)_2NiF_6$ owing to the transition metal contraction and then increases again when going from Ni to the main-group elements.

NMR Spectrum. The ionic nature of $(NF_4)_2MnF_6$ in HF solution was established by its ^{19}F NMR spectrum which was recorded over the temperature range +20 to -75°C. It showed at all temperatures a broad resonance at ϕ -218 (downfield from external $CFCl_3$), characteristic of NF_4^+. The lack of observable NF spin-spin coupling, generally seen for tetrahedral NF_4^+,[16,17] is attributed to the influence of the paramagnetic MnF_6^{2-} anion which can provide rapid relaxation.

Vibrational Spectra. The ionic nature of $(NF_4)_2MnF_6$ in the solid state was established by its vibrational spectra which exhibit the bands characteristic for NF_4^+ [15] and MnF_6^{2-} [18]. Figure 1 shows the infrared spectrum of $(NF_4)_2MnF_6$, compared to that of Cs_2MnF_6. Great difficulties were encountered in obtaining good quality Raman spectra with the blue 4880 Å exciting line of our spectrometer due to strong luminescence[18] (ruby red light emission). However, the principal Raman lines of NF_4^+ [15] and MnF_6^{2-} [18] were observable even under these conditions. The observed vibrational frequencies and their assignments are summarized in Table 3. Since the assignments of NF_4^+ [15] and MnF_6^{2-} [18] are well established, no further discussion is required.

Summary. The present study shows that, in HF solution, solvolysis preempts the metathetical synthesis of NF_4^+ salts containing triply charged MF_6^{3-} anions derived from third row transition metal fluorides. On the other hand, three NF_4^+ salts derived from doubly charged MF_6^{2-} anions are accessible by this method. These salts are $(NF_4)_2TiF_6$,[13] $(NF_4)_2MnF_6$, and $(NF_4)_2NiF_6$.[6] All of them are stable at room temperature, with $(NF_4)_2NiF_6$ possessing the lowest thermal stability. The existence of stable NF_4^+ salts of TiF_6^{2-}, MnF_6^{2-} and NiF_6^{2-} can be explained by the favorable d^0, d^3 (high spin) and d^6 (low spin) electron configurations, respectively, of these anions. The combination of good thermal stability with high active fluorine content (1.485 g per cm^3) renders $(NF_4)_2MnF_6$ a very attractive candidate for solid propellant NF_3-F_2 gas generator compositions.

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Table 1. X-Ray Powder Data for $(NF_4)_2MnF_6$[a]

d obsd	Int.	d calcd	h	k	l
6.21	w	6.21	1	1	1
5.55	vs	5.55	0	0	2
3.49	s	3.49	1	0	3
3.35	s	3.35	3	1	0
2.92	ms	2.92	2	1	3
2.781	ms	2.776	0	0	4
2.436	ms	2.437	3	3	1
2.307	mw	2.302	3	2	3
2.181	s	2.179	4	2	2
2.078	mw	2.078	5	1	0
1.979	mw	1.980	5	0	2/ 4 3 2
1.875	ms	1.873	4	4	0

a Tetragonal, a= 10.60Å, c= 11.10Å, V= 1246.7Å^3, Z= 16/3, ρ calcd = 2.48 g cm^{-3}, CuK_α radiation and Ni filter.

Table 2. Crystallographic Data of $(NF_4)_2MnF_6$ Compared to Those of Other $(NF_4)_2MF_6$ Salts[a]

	Tetragonal unit cell dimensions			Vol/F	calcd density,
	a, Å	c, Å	V, Å^3	Å^3	g/cm^3
$(NF_4)_2TiF_6$[b]	10.715	11.114	1276.0	17.09	2.37
$(NF_4)_2MnF_6$	10.597	11.102	1246.7	16.70	2.48
$(NF_4)_2NiF_6$[c]	10.457	10.953	1197.7	16.04	2.61
$(NF_4)_2GeF_6$[d]	10.627	11.114	1255.1	16.81-	2.59
$(NF_4)_2SnF_6$[e]	10.828	11.406	1337.4	17.91	2.73

a) For all compounds Z = 16/3.

b) Reference 13.

c) Reference 6.

d) Reference 15.

e) Reference 8.

Table 3. Vibrational Spectra of Solid $(NF_4)_2MnF_6$ and Cs_2MnF_6

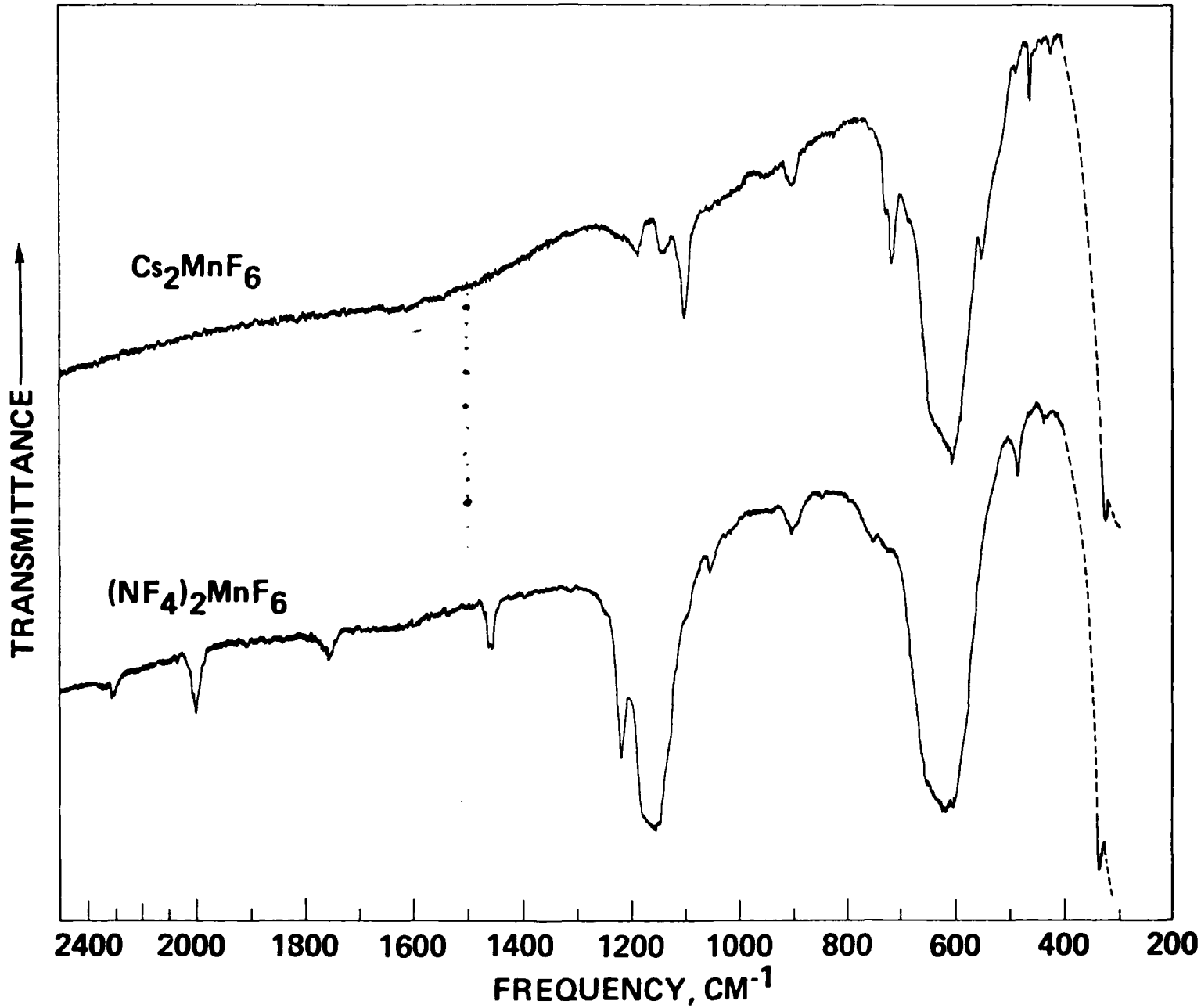
Obsd freq, cm^{-1}, and rel intens[a]				Assignment (point group)[b]	
$(NF_4)_2MnF_6$		Cs_2MnF_6		NF_4^+ (T_d)	MnF_6^{--} (O_h)
IR	RA	IR	RA		
2310vw				$2\nu_3(A_1+E+F_2)$	
2000w				$\nu_1+\nu_3(F_2)$	
1759vw				$\nu_3+\nu_4(A_1+E+F_2)$	
1466w				$\nu_1+\nu_4(F_2)$	
1221mw				$2\nu_4(A_1+E+F_2)$	
		1240sh			$\nu_1+\nu_3(F_{1u})$
		1202vw			
1160vs				$\nu_3(F_2)$	
		1155vw			
1110sh		1116w			$\nu_2+\nu_3(F_{1u}+F_{2u})$
1061vw				$\nu_3+\nu_4(F_1+F_2)$	
915vw		919vw			$\nu_1+\nu_4(F_{1u})$
856vvw	855m			$\nu_1(A_1)$	
760sh		745sh			
735sh		732w			$\nu_2+\nu_6(F_{1u}+F_{2u})$
620vs		620vs		$\nu_4(F_2)$	$\nu_3(F_{1u})$
	593vs		590vs		$\nu_1(A_{1g})$
		569vw			
500vw	505m		502m		$\nu_2(E_g)$
450vw	450w			$\nu_2(E)$	
		381vw			
338s		338s			$\nu_4(F_{1u})$
	304s		304s		$\nu_5(F_{2g})$

(a) uncorrected Raman intensities

(b) the actual site symmetries of NF_4^+ and MnF_6^{--} in $(NF_4)_2MnF_6$ are probably lower than T_d and O_h, respectively, as indicated by the large unit cell ($Z = 16/3$) and the observed slight deviations from the selection rules. However, since the actual site symmetries are unknown, the assignments are given for the idealized point groups.

Diagram Caption

Figure 1. Infrared spectra of solid Cs_2MnF_6 and $(NF_4)_2MnF_6$ recorded at 25° as dry powders pressed between AgCl disks. The broken lines indicate absorption due to the window material.



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APPENDIX K

VIBRATIONAL SPECTRA OF $^{15}NF_4^+AsF_6^-$ AND GENERAL VALENCE FORCE FIELD OF NF_4^+

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Abstract

Samples of $^{14}NF_4AsF_6$ and $^{15}NF_4AsF_6$ were prepared by low-temperature uv-photolysis and their vibrational spectra were recorded. The observed spectra are in agreement with space group P4/n for NF_4AsF_6 and site symmetries of S_4 and C_4 for NF_4^+ and AsF_6^-, respectively. The observed ^{14}N - ^{15}N isotopic shifts were used to compute a general valence force field for NF_4^+.

Introduction

Since the first report [1,2] on the existence of NF_4^+ salts numerous papers [3-25] dealing with NF_4^+ chemistry have been published. The vibrational spectrum of NF_4^+ is well known [5, 7-9, 13-15, 17-19], and its force field has been computed [5,7]. However, the earlier work permitted only computation of an approximate force field, since the F_2 block has two fundamentals and three symmetry force constants. In view of the general interest in the NF_4^+ cation, the computation of a general valence force field was highly desirable. In addition, it was hoped that the vibrational spectra might allow the determination of the space group of NF_4AsF_6.

Experimental

The samples of $^{14}NF_4AsF_6$ and $^{15}NF_4AsF_6$ were prepared by low-temperature uv-photolysis of mixtures of F_2, AsF_5 and $^{14}NF_3$ or $^{15}NF_3$, respectively, in a quartz reactor, using a previously described method [15]. The $^{15}NF_3$ starting material was prepared by glow-discharge of $^{15}N_2$ (99% ^{15}N, Stohler Isotope Chemicals) and F_2 (Rocketdyne), as previously described [26]. Volatile materials were handled in a stainless steel Teflon-FEP vacuum system and solids in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgCl disks in a Wilks mini press. The spectrometer was calibrated by comparison with standard gas calibration points [27,28]. The Raman spectra were recorded on Spex Ramalog and Cary Model 83 spectrophotometers using the 4880Å exciting line and quartz tubes as sample containers. The reported frequencies and isotopic shifts are believed to be accurate to ± 1 and ± 0.1 cm^{-1}, respectively.

Results and Discussion

The sample of $^{15}NF_4AsF_6$ was of high isotopic purity and its vibrational spectra did not exhibit any detectable bands due to the ^{14}N isotope. To determine the ^{14}N - ^{15}N isotopic shifts, the corresponding ^{14}N salt was prepared and studied by vibrational spectroscopy under identical conditions. Since the ^{15}N salt spectra were identical to those previously published for the ^{14}N salt [15], except for the isotopic shifts observed for ν_3 and ν_4 of NF_4^+ the actual spectra are not shown. The observed frequencies, ^{14}N - ^{15}N isotopic shifts and assignments are summariezed in Table 1.

Although the assignments given in Table 1 were made for simplicity for tetrahedral NF_4^+ and octahedral AsF_6^-, the observed splittings of the degenerate modes and deviations from the T_d and O_h selection rules indicate that the actual site symmetries of the NF_4^+ and AsF_6^- ions must be lower than T_d and O_h, respectively. Unfortunately, the exact crystal structure of NF_4AsF_6 is unknown, however, based on its reported x-ray powder diffration data [4], NF_4AsF_6 appears to be isotypic with $PCl_4^+PCl_6^-$ which belongs to space group P4/n (C_{4h}^3, Nr.85) [29,30]. In this space group,the NF_4^+ cation would occupy sites of symmetry S_4. As can be seen from comparison of Tables I and II, the observed NF_4^+ bands agree well with the predictions for S_4 site symmetry, but not with those for D_2 or D_{2d}. Similarly, the deviations from the O_h selection rules, observed for AsF_6^-, are compatible with a site symmetry of C_4 (see Table III), but not with D_{2d}, D_{2h}, D_2 or S_4. Based on these results, alternate probable space groups, such as P4/nmm, $P4_2/n$, $P4_222$, $P4_2/mmc$, P4/mnc $P4_2/mnm$ or P4/m, can be ruled out.

Since the A_1 and E block of tetrahedral NF_4^+ contain only one fundamental vibration each, the values of the corresponding symmetry force constants are uniquely determined. For the F_2 block which contains one stretching and one deformation mode, additional data, such as ^{14}N - ^{15}N isotopic shifts, are needed to allow the calculation of unique values for the three symmetry force constants.

In solid NF_4AsF_6 the F_2 modes of NF_4^+ are split under S_4 site symmetry into one B and one doubly degenerate E mode. Since the isotopic shifts of both modes are very similar (see Table II), weighting of the shifts can be neglected and a simple average was used. It should be pointed out however that in certain NF_4^+ salts, such as NF_4BF_4[31], the ^{14}N - ^{15}N isotopic shifts of the $\nu_3(F_2)$ components can differ by as much as 8 cm^{-1}, thus requiring reliable mode assignments.

As expected from their G matrix elements, the ^{14}N - ^{15}N isotopic shifts of $\nu_1(A_1)$ and $\nu_2(E)$ were found to be zero within experimental error. Those of $\nu_3(F_2)$ and $\nu_4(F_2)$ were measured to be 29.25$\pm$ 0.25 and 1.8$\pm$ 0.1 cm^{-1}, respectively. These values were supported by preliminary measurements on $^{14}NF_4BF_4$ and $^{15}NF_4BF_4$[31] which shows very similar averaged isotopic shifts for ν_3 and ν_4.

For the computation of the general valence force field of NF_4^+ the frequencies and isotopic shifts listed in Table 4 were used. For the F_2 block, the possible ranges of the two diagonal symmetry force constants F_{33} and F_{44} and the ^{14}N - ^{15}N isotopic shifts of ν_3 and ν_4 were computed as a function of the interaction constant F_{34} by trial and error and by the use of the expressions previously reported [32] for the calculation of extremal force constant solutions. The results of these calculations are shown in Figure 1. The observed ^{14}N - ^{15}N isotopic shifts were used to graphically select the correct F_2 block force field. The isotopic shift of ν_4 was preferred because, due to its smallness, anharmonicity corrections should be unimportant [33].

Since the slopes of the $\Delta\nu_3$ and $\Delta\nu_4$ versus F_{34} plots have opposite signs, the $\Delta\nu_4$ range might be used as a rough estimate for the anharmonicity correction

required for $\Delta\nu_3$. Figure 1 indicates an anhormonicity correction of about 1 cm^{-1} for $\Delta\nu_3$, which is in line with previous estimates for similar molecules, such as NF_3 [34].

The general valence force field and the potential energy distribution (PED) of NF_4^+ are summarized in Table 4. The PED indicates significant mixing of S_3 and S_4, as expected [32, 36] for a strongly mass coupled system [32, 36]. The close agreement between the general valence force field of this study and the previously reported [5, 7] approximate force field is in line with Pfeiffer's analysis [37] which showed that for similar molecules the method of "stepwise coupling" gives the best agreement with the general valence force field values. A comparison of the NF stretching force constant of NF_4^+ (6.15 mdyn/Å with those and the NF bond distances of FNO (f_r = 2.15 mdyn/Å, r_{NF} = 1.512Å) and NF_3(f_r = 4.31 mdyn/Å, r_{NF} = 1.365 Å) [35] suggests for NF_4^+ an unusually strong and short (r ~ 1.24Å) NF bond.

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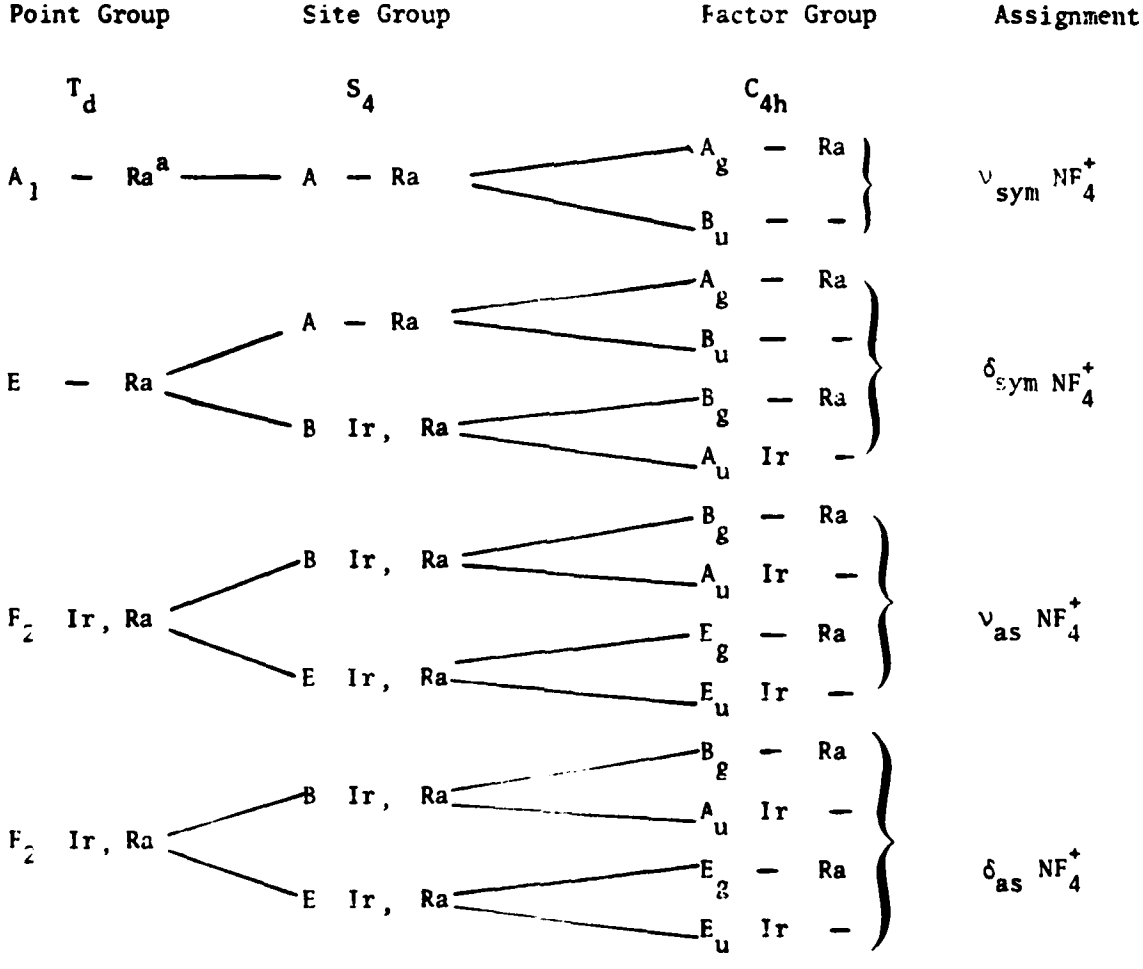
Table 1. Vibrational Spectra of $^{14}NF_4AsF_6$ and $^{15}NF_4AsF_6$

$^{14}NF_4AsF_6$		$^{15}NF_4AsF_6$		Assignments (point group)[a]		$\Delta\nu$ ^{14}N - ^{15}N	
IR	RA	IR	RA	$NF_4^+(T_d)$	$AsF_6^-(O_h)$		
2360 vvw 2310 vw		2310 vvw 2253 vw		$2\nu_3(A_1+E+F_2)$			
2012 sh 1997 w		1984 sh 1969 w		$\nu_1+\nu_3(F_2)$			
1780 sh 1765 vw 1760 sh		1732 vw		$\nu_3+\nu_4(A_1+E+F_2)$			29.2±1.8
1457 sh 1455 w		1455 sh 1451 w		$\nu_1+\nu_4(F_2)$			?
1398 vw		1398 vw			$\nu_1+\nu_3(F_{1u})$		
1290 vw		1290 vw			$\nu_2+\nu_3(F_{1u}+F_{2u})$		
1221.9 mw		1218.2 mw		$2\nu_4(A_1+F+F_2)$			1.85
1165 vs, br	1165.0 (1) 1152.9 (0.6)	1135 vs, br	1136.0 (1) 1125.4 (0.6)	$\nu_3(F_2)$		29.0 29.5	29.25±0.25
1056 sh 1052 vw		1054 sh 1050 vw		$\nu_2+\nu_4(F_1+F_2)$			
	882 (0+) 848.2 (7.3)		882 (0+) 848.2 (7.3)	$2\nu_2(A_1+A_2+F)$ $\nu_1(A_1)$			
826 vw		826 vw			$\nu_2+\nu_6(F_{1u}+F_{2u})$		
710.0 vs, br	704.5 (1.5)	710 vs, br	704.5 (1.5)		$\nu_3(F_{1u})$		
685 sh	685.4 (10)	685 sh	685.4 (10)		$\nu_1(A_{1g})$		
615.5 s	615.5 (2.6)	611.5 s	611.4 (2.6)			1.8, 1.9	1.85±0.1
609.0 s	609.0 (5.2)	607.3 s	607.2 (5.2)	$\nu_4(F_2)$	$\nu_2(E_g)$	1.7, 1.8	
579 w	578.5 (1.2)	579 w	578.?				
	445.0 (1.9) 441.6 (2.0)		444.9 (1.9) 441.5 (2.0)	$\nu_2(E)$		0.? ± 0.1	
395 s		395 s			$\nu_4(F_{1u})$		
	369.6 (3.6)		369.6 (3.6)		$\nu_5(F_{2g})$		

(a) The site symmetry of NF_4^+ and AsF_6^- in NF_4AsF_6 is S_4 and C_4, respectively (see text). However, since reliable assignments for the nearly degenerate vibrations cannot be made for S_4 and C_4, the observed spectra were assigned in point group T_d and O_h, respectively.

Table II. Correlation Table for the Internal Vibrations of NF_4^+ in NF_4AsF_6 for Space Group P4/n and Z=2



(a) Spectral activity

Table III. Correlation Table for the Internal Vibrations of AsF_6^- in NF_4AsF_6 for Space Group P4/n and Z = 2

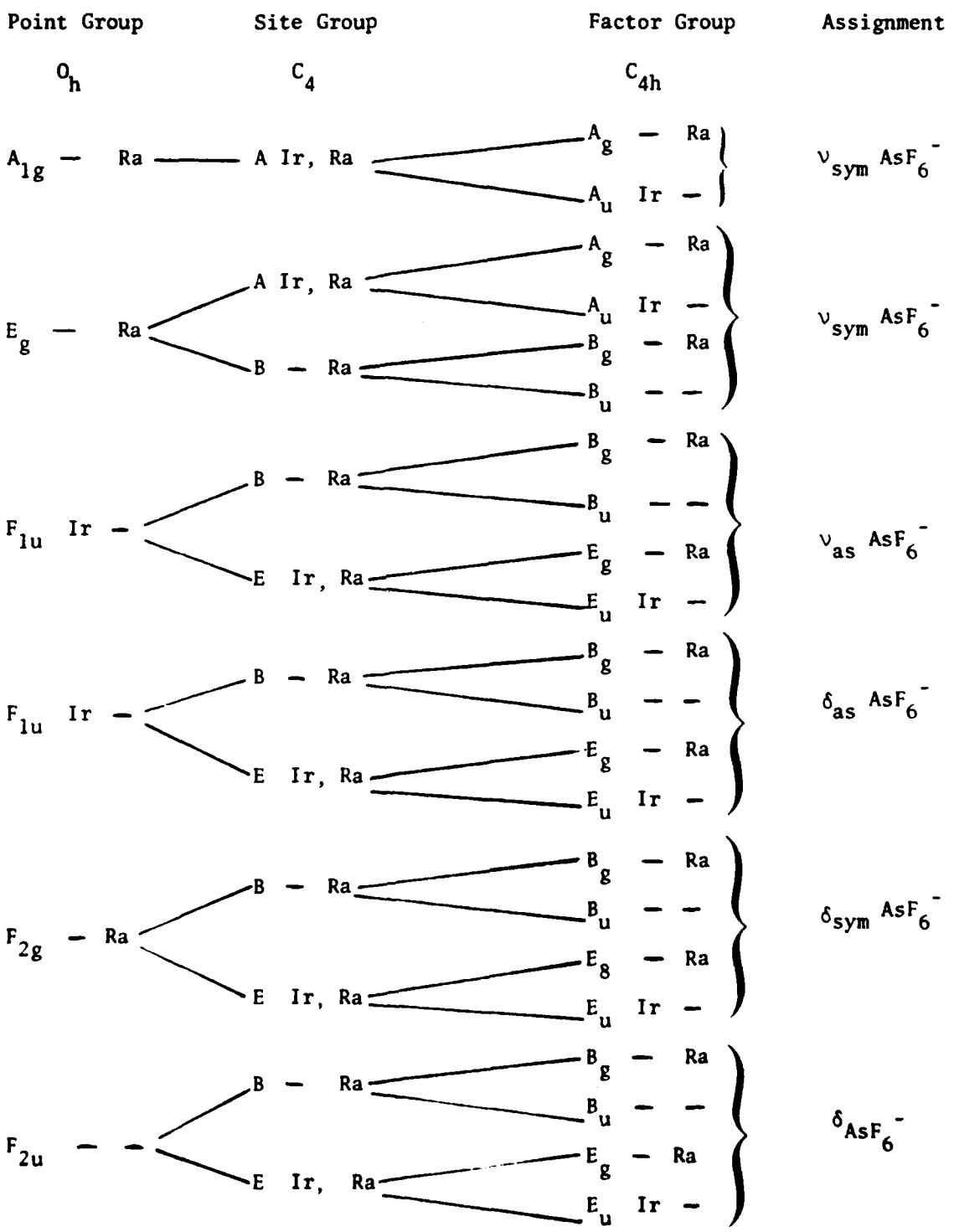


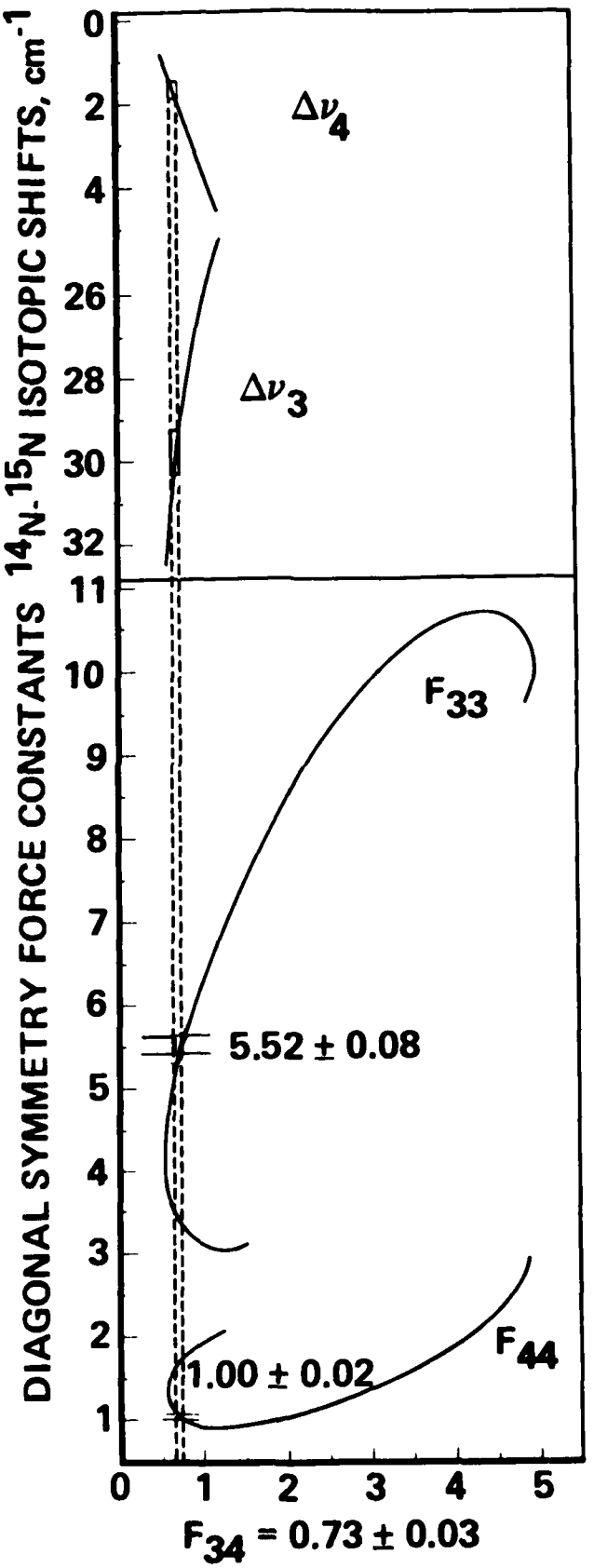
Table 4. Frequency Values, ^{14}N-^{15}N Isotopic Shifts (cm^{-1}), General Valence Force Field[a] and Potential Energy Distribution for NF_4^+

		$\nu^{14}NF_4^+$	$\nu^{15}NF_4^+$	$\Delta\nu$	Symmetry Force Constants	PED
A_1	ν_1	848.2	848.2	0	$F_{11} = f_r + 3f_{rr} = 8.053$	
E	ν_2	443.3	443.3	0	$F_{22} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'} = 0.733$	
F_2	ν_3	1158.95	1129.7	29.25 ± 0.25	$F_{33} = f_r - f_{rr} = 5.52 \pm 0.08$	$96F_{33} + 43F_{44} - 39F_{34}$
	ν_4	611.15	609.35	1.8 ± 0.1	$F_{44} = f_\alpha - f_{\alpha\alpha'} = 1.00 \pm 0.02$	$15F_{33} + 67F_{44} + 18F_{34}$
					$F_{34} = \sqrt{2}\,(f_{r\alpha} - f_{r\alpha'}) = 0.73 \pm 0.03$	
					$f_r = 6.153 \pm 0.1$	
					$f_{rr} = 0.633 \pm 0.03$	

(a) Stretching, bending and stretch-bend interaction force constants have units of mdyn /Å, mdyn /Å radian^2 and mdyn /Å radian, respectively.

Diagram Caption

Figure 1. F_2 block force field (mdyn/Å) of NF_4^+. The diagonal symmetry force constants and ^{14}N - ^{15}N isotopic shifts are plotted as a function of the interaction constant F_{34}. The rectangles delineate the observed ^{14}N - ^{15}N isotopic shifts and their uncertainties. The broken vertical and solid horizontal lines indicate the resulting force constant ranges.


DIAGONAL SYMMETRY FORCE CONSTANTS ^{14}N-^{15}N ISOTOPIC SHIFTS, cm^{-1}
$\Delta\nu_4$
$\Delta\nu_3$
F_{33}
F_{44}
5.52 ± 0.08
1.00 ± 0.02
F_{34} = 0.73 ± 0.03
0
2
4
26
28
30
32
11
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5

APPENDIX L

ASSAY OF NF_4^+ SALTS OF COMPLEX FLUORO ANIONS

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ABSTRACT

The NF_4^+ content of complex fluoro anion salts is reliably determined by quantitative measurement of the NF_3 evolved during hydrolysis using gasometric and chromatographic methods. The metal central atoms of the anions were determined by different techniques, including atomic absorption and x-ray fluorescence spectroscopy and gravimetry. The use of several semiquantitative methods and of qualitative methods for the detection of impurities or polyanions is briefly discussed.

APPENDIX M

Analysis of the Electron Paramagnetic Resonance Spectra of $^{14}NF_3^+$ and $^{15}NF_3^+$

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ABSTRACT

Electron paramagnetic resonance spectra of $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$ were analysed in detail using a computer simulation. The ^{14}N or ^{15}N hyperfine tensors were assumed to be axially symmetric, and parallel to the g-tensor. Three equivalent ^{19}F hyperfine tensors were used in which the angle (α) of the Z-component was allowed to vary with respect to the molecular symmetry axis. Values of the hyperfine couplings were in reasonable agreement with those derived from an approximate analysis of the spectra. The best value of α was found to be $15\pm0.5^{\circ}$ indicating that the planarity of XF_3 radicals decreases in the sequence: $NF_3^{+\cdot}$, $CF_3\cdot$, $BF_3^{-\cdot}$. Some variation in the couplings in $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$ was observed, and may be the result of slight molecular oscillations.

Hyperfine Couplings of NF_3^+ (MHz)

	$^{14}NF_3^+$(1)	$^{14}NF_3^+$(2)	$^{15}NF_3^+$	a(^{15}N)/-1.403
$A_N(\perp)$	113.0	100.0	-135.0	96.2
$A_N(\parallel)$	317.3	317.0	-463.3	330.2
A_N iso	181.1	172.3	-244.4	174.2
$A_F(x)$	(-)155.0	(-)175.0	(-)155.5	
$A_F(y)$	(-) 80.0	(-) 80.0	(-) 84.5	
$A_F(z)$	879.3	879.0	912.8	
A_F(iso)	214.8	208.0	224.3	
$g(\perp)$	2.0030	2.0030	2.0065	
$g(\parallel)$	2.0060	2.0060	2.0060	
g iso	2.0050	2.0050	2.0063	
α	15.5°	14.5°	14.5°	